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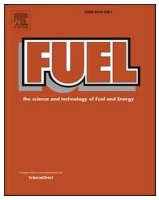

Full Length Article

Flexible methanol production process using biomass/municipal solid waste and hydrogen produced by electrolysis and natural gas pyrolysis

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ABSTRACT

Biomass-derived liquid fuels with low greenhouse gas emissions are an integral part of decarbonization plans. Three pathways for enhancing production of methanol from biomass and municipal solid waste (MSW), natural gas, and renewable electricity are explored using hydrogen produced from water electrolysis, natural gas pyrolysis, or combinations of these inputs. A combined electrolysis and natural gas pyrolysis process is designed to be flexible, changing operation modes depending on the cost of feedstocks (i.e. electricity and natural gas). A techno-economic analysis is performed to assess and compare the economic attractiveness of these processes. Hydrogen produced from natural gas pyrolysis could potentially be more economically attractive than electrolytic hydrogen using renewable electricity. Moreover, natural gas pyrolysis CO_2 emissions could be substantially lower than emissions from conventional steam methane reforming (e.g., CO_2 emissions which are 25 % or lower compared to CO_2 emission from steam methane reforming). Hydrogen enhancement of the methanol production process results in increase of around a factor of two in carbon conversion efficiency (e.g. from 44% to 94 %). Methane pyrolysis shows high economic potential assuming the technical challenges to its commercialization are successfully addressed. Given an installed cost of electrolyzer of 1000 $/kW, electricity price of 50 $/MWh, natural gas price of 5 $/GJ and 100 $/ton selling price of carbon black, the natural gas pyrolysis design results in the lowest methanol production cost. Our analysis indicates that methanol could be produced in a price range of 300–1000 $/ton depending on feedstock price (particularly electricity) and the chosen process.

1. Introduction

With the challenging goal of greenhouse gas emissions reduction, there is increasing interest in the production of hydrogen, liquid fuels, and chemicals from renewable feedstocks and electricity generated from carbon-neutral sources. The dual challenge of increasing worldwide energy use and growing concern over global warming has generated interest in the use of biomass and municipal solid waste (MSW) as sustainable carbon and energy sources. Biomass is rich in carbon and therefore can be used to produce sustainable liquid fuels such as methanol and Fischer-Tropsch (FT) fuels. Moreover, the continuous decline in the cost of renewable power [1] has sparked interest in integrating renewable power into the design of chemical processes. Such fuel can be categorized as a renewable fuel since it is produced from sustainable sources such as biomass/ MSW and renewable electricity.

Methanol is a feedstock chemical and a high-octane fuel that is considered an important alternative fuel for vehicles [2]. If produced from renewable carbon in biomass or MSW, it can replace conventional fossil fuels and provide both lower air pollution and greenhouse gas emissions in the transportation sector. Alternatively, methanol to gasoline (MTG) could be used for manufacturing gasoline-equivalent fuels. The use of methanol that is produced from biomass and MSW can also

Abbreviations: ASU, Air Separation Unit; BE, Biomass and Electricity to Liquid Process using Electrolysis; BP, Biomass and NG Pyrolysis to Liquid Process; BPE, Biomass and NG Pyrolysis and Electrolysis to Liquid Process; BTL, Conventional Biomass to Liquid (i.e., Methanol) Process; CRF, Capital Recovery Factor; FCI, Fixed Capital Investment; HHV, Higher Heating Value; LCOMeOH, Levelized Cost of Methanol; LHV, Lower Heating Value; ME, MSW and Electricity to Liquid Process using Electrolysis; MP, MSW and NG Pyrolysis to Liquid Process; MPE, MSW and Electrolysis and NG Pyrolysis to Liquid Process; MSW, Municipal Solid Waste; NG, Natural Gas; SOEC, Solid Oxide Electrolysis Cell; TCI, Total Capital Investment; WC, Working Capital; WGS, Water Gas Shift reaction; WHB, Waste Heat Boiler.

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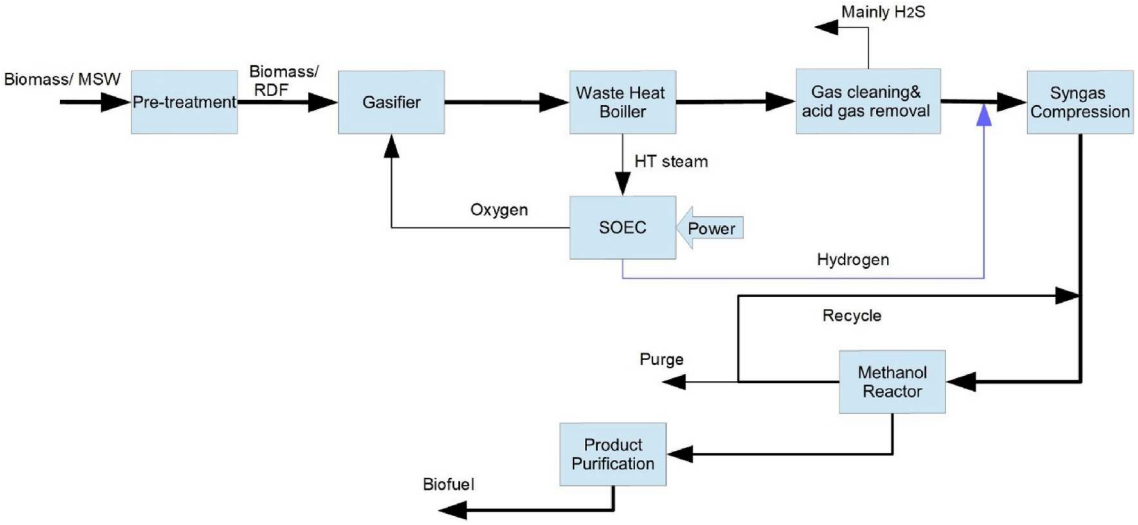

Fig. 1. Block flow diagram of BE/ME process, where hydrogen and oxygen produced from high-temperature steam-electrolysis is added.

reduce greenhouse gas in the industrial sector since methanol is used as a precursor to other commodity chemicals, such as formaldehyde, acetic acid, etc.

The production of methanol from gasification of biomass to liquids (BTL) has been described by several groups using various gasifiers [3–5]. These processes can critically suffer from low carbon efficiency and thus more than 50 % of carbon in biomass exits the process as CO_2. As for biomass, MSW is poor in hydrogen and conventional wisdom suggests shifting CO to CO_2 in a Water-Gas-Shift (WGS) reaction, increasing the H_2 content of the syngas at the expense of producing the undesirable component CO_2. To increase the carbon efficiency of the process without production of CO_2, external hydrogen needs to be added to increase the hydrogen content of the gasification syngas. This hydrogen can come from any source. In this paper, the focus is on natural-gas pyrolytic hydrogen and electrolytic hydrogen. The concept of adding electricity (through electrolytic hydrogen production or, to a lesser extent, through natural gas pyrolysis) to biomass to fuel processes is relatively new and has gained attention in recent years [6–10]. In all these studies, external hydrogen addition increases the carbon efficiency of the process by roughly doubling the produced fuel for a given input of biomass.

There have also been investigations into the use of MSW gasification to produce fuels such as methanol [11–15]. Most studies in the literature on MSW gasification deal with modeling aspects and it has been difficult to find sufficient experimental information. What is common among these studies is that production of fuel from MSW has the benefit of gate fee or tipping fee which is non-existent for biomass (explained more in section 5.4). This gives MSW a competitive edge to be used as a gasifier feedstock for fuel production. However needless to say that mainly in Europe, produced fuel from MSW might not be considered renewable and thus the plant may not be entitled to certain supporting mechanisms. There are few investigations suggesting the addition of hydrogen to MSW to methanol process for enhanced carbon efficiency [11,12,16]. Salladini et al. [11] investigated the waste to methanol process with and without hydrogen addition. By addition of external hydrogen from an alkaline electrolyzer, the production of methanol doubled for the same amount of waste feedstock. The estimated production cost of methanol was 348 €/ton for a plant with a methanol production capacity of 471 ton/d.

The splitting of methane to produce hydrogen and elemental carbon has been pursued for many decades for producing carbon black but has not yet been successfully commercialized to produce low-carbon hydrogen to reduce greenhouse gas emissions. However, there is growing interest in pursuing this pathway for producing low-carbon hydrogen and there are recent efforts to commercialize methane pyrolysis (e.g. BASF [17], Monolith [18], C-Zero [19], Ekona [20]). The methane pyrolysis process using renewable power or hydrogen as a heating source can be considered a low-carbon emission process to produce hydrogen.

To reduce the production cost of methanol, we have also investigated a feed-flexible process. Flexibility is enabled by a process that can adjust between operating modes to produce the lowest cost fuel depending on the market price of feedstocks (natural gas and electricity). There are investigations on flexibility in methanol production in the literature [10,21]. Butera et al. [10] investigated several designs for flexible production of methanol, co-production of methanol and electricity, or production of electricity from biomass by coupling biomass gasification and solid oxide cells (SOCs). In the flexible process that we are considering, continuous and steady-state operation of methanol synthesis reactor is considered with constant methanol production year-around. Flexibility is obtained by adjusting the means to produce oxygen and hydrogen required by the process to produce the lowest cost methanol and considering hydrogen production from electrolysis and/or natural gas pyrolysis.

Starting with biomass/ MSW, natural gas, and renewable power, one conventional biomass to liquid (BTL) case for producing methanol and three hydrogen-enhanced cases have been investigated in this paper. The first two enhanced cases differ in the method of producing H_2, either through natural gas pyrolysis- or through steam electrolysis through a solid oxide electrolysis cell (SOEC). The third enhanced case, which has both pyrolytic and electrolytic hydrogen addition is proposed for increased flexibility. When cheap renewable electricity is available, steam electrolysis is used for O_2 and H_2 production. At times with high electricity prices, natural gas is used in a pyrolysis reactor to produce H_2 and an air separation unit (ASU) is used for O_2 production. For the objective of this paper, it is assumed that the methanol production is constant, and the required hydrogen can be fully produced by either the pyrolysis or electrochemical plants. As a consequence, the peak hydrogen production capability of the plant is twice that which would be required to operate the methanol reactor.

All plant configurations analyzed in this study are based on thermochemical conversion of biomass/MSW to synthesis gas (consisting of H_2 and CO) via gasification and later catalytic conversion of synthesis gas to methanol.

One of the main focuses of the present study is the use of a consistent framework to compare the Levelized cost of production of methanol (LCOMeOH) with low carbon emissions and from renewable sources. Another lies in the use of pyrolytic hydrogen in the methanol synthesis process and subsequent cost estimation. While Steinberg [22] has

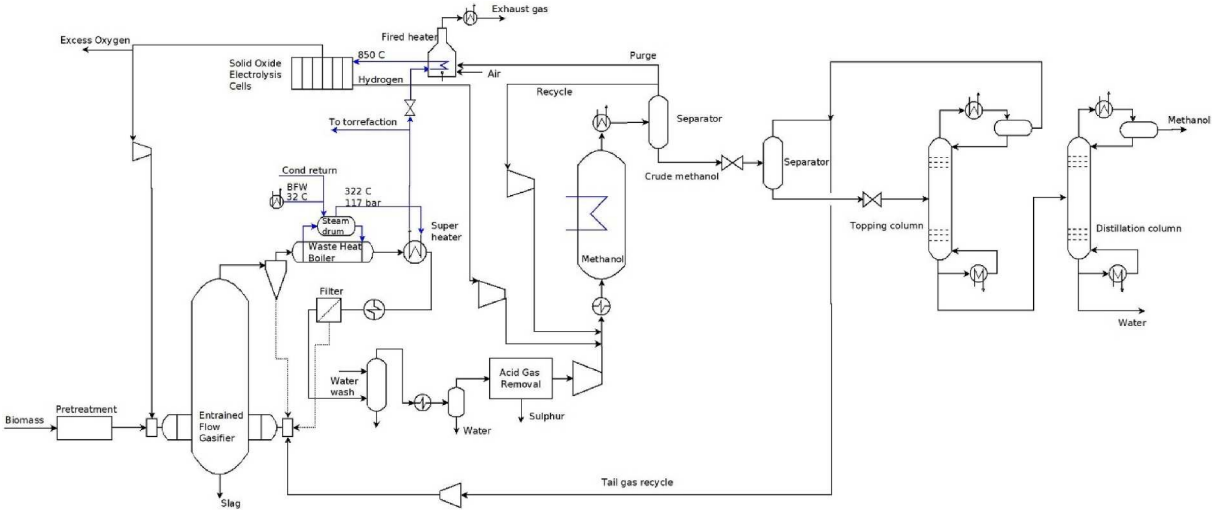

Fig. 2. Process flow diagram of BE/ME process, where hydrogen and oxygen produced from high-temperature steam-electrolysis is added.

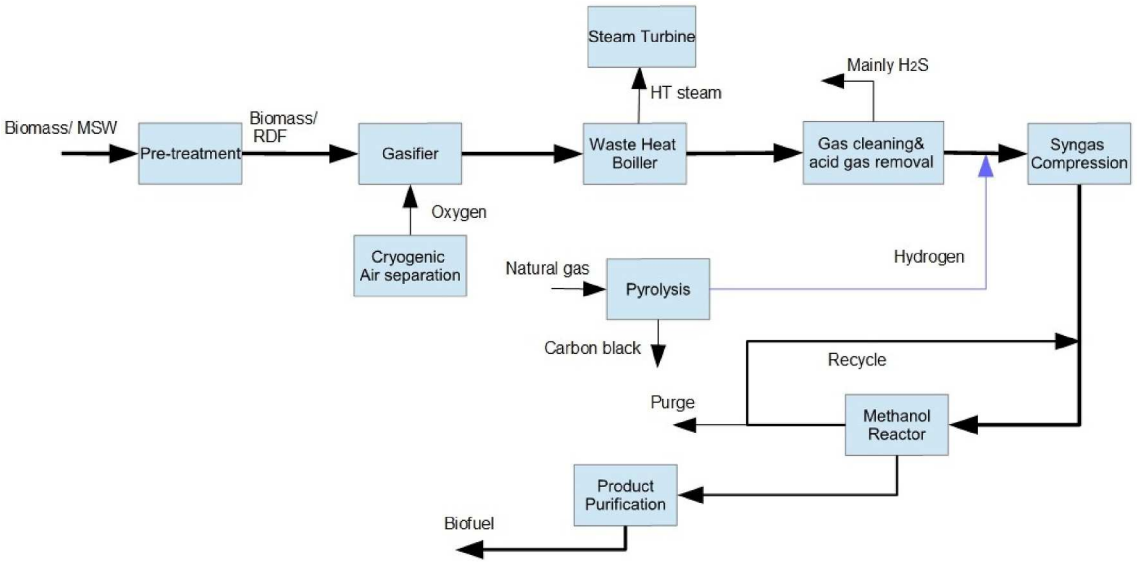

Fig. 3. Block flow diagram of BP/ MP process, where hydrogen produced from natural gas pyrolysis is added.

investigated the integration of pyrolytic hydrogen to convert waste CO_2 from coal-fired power plants to methanol, to the best of our knowledge, no paper has yet investigated the process integration of pyrolytic hydrogen in methanol synthesis. Moreover, a flexible process is proposed which combines natural gas pyrolysis and electrolytic hydrogen to benefit from availability of cheap feedstocks.

2. Process concepts

Because of the low carbon efficiency of the conventional Biomass to Liquid (BTL) process, our focus has been to analyze process designs where external hydrogen is added to the process. A common feature between all the designs is the same methanol production rate (48 ton/ hr). And as biomass or MSW is the only source of carbon in these designs, this implies that their carbon input rates are also the same. Another common feature is that the acid gas removal section is mainly to remove H_2S to ppm level [23]. While in the conventional BTL process a high CO_2 capture rate (i.e., 90 %) in the acid gas removal is needed, in hydrogen-enhanced designs the acid gas removal is mainly to remove H_2S. However, the absorption process (here using Selexol) in the acid gas removal unit, 5 % CO_2 is also removed. Physical absorption is chosen here for absorbing H_2S because of its high partial pressure.

2.1. Biomass/ MSW and electricity to liquid process using electrolysis (BE or ME)

To overcome the low carbon efficiency of the BTL process, electrolytic H_2 is added. We refer to this process as the "BE/ME process." A block flow diagram of the BE/ME process is shown in Fig. 1 and a more detailed process flow diagram is shown in Fig. 2. The biomass is pretreated to make it suitable for Entrained Flow gasification (EFG). In the case of MSW, the feedstock is pretreated to make refuse-derived-fuel (RDF). EFG technology is a suitable technology to produce fuel due to the high gasification temperature (1600 °C) which results in relatively clean and tar-free syngas. The oxygen produced from the solid oxide electrolysis cell (SOEC) is used as an oxidant in the gasifier, thereby dropping the need for a cryogenic Air Separation Unit (ASU). The steam for the SOEC is produced in the waste heat boiler (WHB) and superheated to about 850 °C in a fired heater which burns the purge stream from the methanol reactor.

The hot and reactive syngas out of the gasifier is quenched in a WHB to a temperature where the gas is chemically stable and the shift

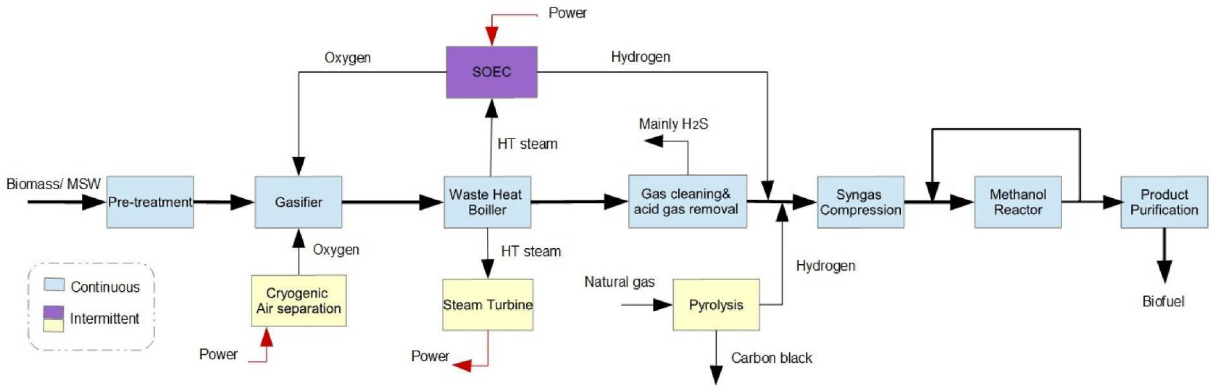

Fig. 4. Block flow diagram of BPE/MPE process, where hydrogen is produced from natural gas pyrolysis and/or Electrolysis. The required O_2 is produced in ASU or SOEC.

Table 1
Elemental composition of RDF and Biomass (wt%).

	RDF	Biomass
Carbon	52.11	51.8
Hydrogen	7.4	6.04
Nitrogen	0.85	0.17
Sulfur	0.46	0.09
Chlorine	0.07	–
Oxygen	39.11	41.9
LHV (MJ/kg) (5 % wet)	19.6	18.1

towards production of CO_2 is not favored. The generated syngas typically has impurities such as NH_3, HCN (Hydrogen Cyanide), H_2S, COS (Carbonyl Sulfide), and HCl (Hydrogen Chloride), in addition to volatile metals and dust [24]. Components like COS and HCN are hydrolyzed to form H_2S, NH_3, and CO_2 over a catalyst [9]. The syngas then enters a water-wash unit to be cleaned of particles and ammonia before entering the acid gas removal unit. Unlike the acid gas removal unit in a conventional BTL process where the target is to remove both H_2S and CO_2, the purpose here is to remove H_2S. Nevertheless, it is assumed that 5 % CO_2 is co-absorbed with H_2S and taken out of the process.

The adjustment of the syngas stoichiometric ratio (**M** in Eq. 5 below) is done solely by injection of enough H_2 from the electrolysis unit. The hydrogen from the SOEC is added after the gas cleaning section. Thereafter the dry and clean syngas is compressed to 80 bar and mixed with recycle stream and heated to a temperature of ca 220 °C before entering the methanol synthesis reactor. The raw methanol out of the reactor is sent to separation section to separate methanol to a purity of 99.5 %. Recirculating the tail gas stream from the topping column to the gasifier results in improved carbon efficiency of the process.

The processing steps for MSW to liquid fuel are the same except the pre-treatment where MSW is pretreated to make refuse-derived-fuel (RDF) (explained in section 3.2).

2.2. Biomass/MSW and NG pyrolysis to liquid process (BP or MP)

Like the BE/ME process described above, the BP/MP process refer to biomass /pyrolysis or MSW / pyrolysis to methanol. The BP and MP process configurations also boost methanol production through hydrogen enhancement, where in this case the hydrogen is produced in a natural gas pyrolysis reactor. The main differences between BP and the BE designs lie in the method of provision of H_2 and O_2. In the BP/MP process, the oxygen required in the gasifier is supplied by an ASU while the hydrogen is produced in a natural gas pyrolysis unit. Moreover, the produced carbon in BP and MP process counts as a source of revenue or alternatively it could be easily sequestered. The block flow diagram of the BP/ MP process is shown in Fig. 3 and a more detailed process flow diagram is shown in Fig. 17 (in the Appendix). While in the BE/ME design, the steam generated in the WHB is sent to SOEC, in this design, steam is sent to a steam turbine for power generation. The generated power in the steam turbine is enough to power the ASU. The generated steam in the WHB is at 117 bar and a temperature of 730 °C. In case where it is sent to the SOEC, the pressure is reduced to 40 bar to meet the pressure limitations of SOEC. In case where steam is sent directly to the steam turbine with a back pressure of 5 bar, the produced power is about 13 MW which is larger than the required power in the ASU (which is 10.5 MW as given in Table 2). Specific power consumption of 0.4 kWh/kg O_2 is assumed for the ASU [25]. Like the previous design, no CO_2 separation is considered here, and instead, the adjustment of the syngas stoichiometric ratio (**M** in Eq. 5 below) is done by injection of enough H_2 from the pyrolysis unit. The acid gas removal section is mainly to remove H_2S. It is assumed that 5 % CO_2 is removed from the process in the acid gas cleaning section. The raw methanol out of the reactor is sent to distillation unit to separate methanol to a purity of 99.5 %. Recirculation of the tail gas stream from the topping column to the gasifier results in improved carbon efficiency of the process. To avoid the accumulation of inert components in the synthesis loop, a purge stream is sent to a fired heater. The main difference between using MP and BP processes is the pretreatment step where MSW is processed into RDF (further discussed in section 3.2).

2.3. Biomass/MSW and electrolysis and NG pyrolysis to liquid process (BPE/MPE)

To take advantage of periods with low-priced electricity and natural gas, a flexible process scheme is proposed which is a combination of the designs described above. The biomass -pyrolysis- electrolysis (BPE) process differs from the BE and BP processes in the way the H_2 and O_2 are produced. When cheap electricity is available, SOEC produces O_2 and H_2 for the process. At times when electricity is expensive, ASU is used to provide O_2 and natural gas pyrolysis produces clean H_2 and elemental carbon. Solid carbon can be disposed of/sequestered much easier than CO_2, or beneficially used, thus the pyrolysis process has an important potential advantage compared to steam or autothermal reforming of natural gas for hydrogen production. The block flow diagram of the combined process is shown in Fig. 4 where intermittent and continuously operated units are distinguished by distinct color codes. The core of the process where units run continuously is shown in blue. The intermittent units which vary depending on the operation mode are shown in yellow (BP) and purple (BE). The continuous units are run without interruptions (i.e., 8000 h in a year), while the intermittent units adjust according to the electricity price. The factors that dictate change between intermittent units are mainly natural gas price, electricity price and its duration. If electricity price is above/below a certain value (which decides high/low electricity price) and for a minimum

Table 2
Technical comparison of proposed concepts.

	Conventional BTL	Enhanced BTL		MSW to Liquid	
	BTL	BE (biomass)	BP (biomass)	ME (MSW)	MP (MSW)
Plant capacity (MWth)	418	197	197	211	211
Biomass/RDF (5 % wet) (tonne/hr)	83.4	39.2	39.2	38.7	38.7
Carbon conversion per pass (%)	50.8	48.7	48.7	46.3	46.3
Carbon efficiency (overall) (%)	44.3	94.3	94.3	94.6	94.6
Thermal efficiency (%)	59	50	51	51	52
Methanol production (tonne/hr)	48.4	48.4	48.4	48.4	48.4
Required power in SOEC (**MWh**) & (MWh/tonne MeOH)	–	**171** & 3.5	–	**162** & 3.3	–
Required power in ASU (**MWh**) & (MWh/tonne MeOH)	**21** & 0.44	–	**10.5** & 0.22	–	**11.9** & 0.24
Steam to SOEC (tonne/tonne MeOH)	–	1.16	–	1.10	–
Natural gas (tonne/hr)	–	–	25.54	–	24.16
Steam to WGS (tonne/tonne MeOH)	0.24	–	–	–	–
Recycle flow to the reactor (tonne/tonne MeOH)	1.38	1.50	1.50	2.14	2.14
Recycle stream compositions (mol%)					
H_2	71.5	72.2	72.2	64.0	64.0
CO	8.6	7.5	7.5	7.1	7.1
CH_3OH	0.6	0.6	0.6	0.6	0.6
CO_2	15.3	16.3	16.3	14.5	14.5
N_2	4.0	3.4	3.4	13.7	13.7

duration (for example at least 3 h) then the respective high/low operation mode will activate. The electricity price forecasts can be obtained from day-ahead markets or weekly/monthly electricity price profiles. More explanation on the effect of duration of high/low electricity price on the methanol production cost is provided in section 5.5. A more detailed process flow diagram is shown in Fig. 18 in the appendix.

3. Process modeling and simulation

Aspen HYSYS® V12 is used as the simulation tool to simulate the process flowsheets in this study. The assumed woody biomass and RDF [26] elemental compositions are given in Table 1. The wet biomass is assumed to have 40 % moisture content which is reduced to 5 % after pretreatment (involving drying and torrefaction). It is also assumed that RDF has 5 % moisture content after pretreatment. The heat of formation of biomass and RDF is based on the method of Burnham [27] using the elemental composition given in Table 1. The required molar heat of formation for biomass and RDF is specified to be $-5.2{\cdot}10^5$ kJ/kmol and -5.3×10^5 kJ/kmol, respectively, with an arbitrary molar mass of 100.1 kg/kmol for both biomass and RDF. The Lower Heating Value (LHV) of RDF (5 % wet) is 19.6 MJ/kg and the LHV of dry biomass (5 % wet) is 18.1 MJ/kg.

Based on the average biomass plant sizes considered in the literature, a plant size of 200 MW_{th} (based on LHV of biomass) is considered for the hydrogen-enhanced cases, resulting in a plant production capacity of 48 tonne MeOH/hr (384,000 tonne MeOH /yr). The size of the BTL plant is chosen to match the 48 tonne MeOH /hr production, which results in a 418 MWth plant (based on LHV of biomass).

3.1. Biomass pretreatment

The biomass pretreatment step includes drying, torrefaction (to improve grindability of the biomass), and grinding to a particle size suitable to EFG. The torrefaction unit is integrated with the gasifier which results in no loss of carbon [28]. The pretreatment step uses steam from the steam system within the process. The thermal power required in the drying step is assumed to be 2.8 GJ per tonne of evaporated water [9]. About 8 % of the superheated steam out of the WHB is sent to the torrefaction and drying unit.

3.2. MSW pretreatment to RDF

Municipal solid waste is defined as household, commercial, and industrial solid waste [13]. MSW has the potential to be used as a gasifier feedstock because it has a heating value that is as high as most biomass feedstocks [13]. The use of MSW for power or fuel production is appealing due to pre-existing collection/transportation infrastructure and tipping fee (which is equivalent to a negative feedstock price) that is non-existent for biomass resources. However, MSW is a heterogeneous feedstock holding materials that vary in size, composition, and shape. Feeding MSW directly to the gasifier in an as received condition is challenging. To make MSW suitable as a gasifier feedstock, it is pre-processed into refuse-derived-fuel (RDF). MSW pre-treatment to produce RDF involves several steps such as size reduction, screening, sorting, and, in some cases pelletization. A typical RDF production line [13] is shown in Fig. 5. Higher heating value, more homogenous physical and chemical compositions, less emissions, less oxygen consumption, and simpler storage, handling, and transportation are the key advantages of converting MSW to RDF [13]. However, there is a trade-off between the increased costs of producing RDF from MSW and potential cost

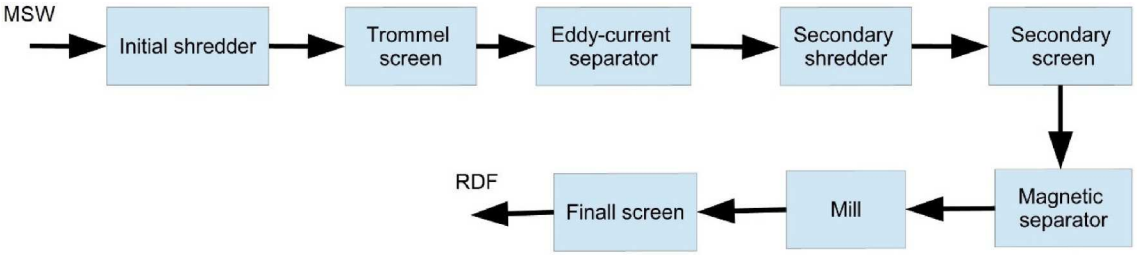

Fig. 5. Typical RDF production line [13].

reductions in gasifier design and operation [13]. On average, MSW to RDF conversion retains 75 %–85 % of the weight and 80 %–90 % of the heating value [13]. Needless to mention that suitability of use of RDF as EFG feed needs to be tested and proved. There is also potential for blending biomass with RDF [29].

3.3. Gasification

An Entrained Flow Gasification (EFG) is considered for syngas production. EFG technology shows some advantages over other gasification types, such as: melting of ash and thermal cracking of tars due to elevated temperatures, higher conversion of tars and higher conversion of carbon, simpler and cheaper design of gas cleaning downstream the gasifier, etc. The gasifier is modeled by two reactors: in the first one biomass/RDF are decomposed into elements with a stoichiometry given by the biomass/RDF elemental composition (Table 1). Then the decomposed biomass/RDF combined with oxygen enter the Gibbs reactor and the equilibrium composition is calculated by minimizing the Gibbs free energy. The temperature of the gasifier is adjusted at 1600 °C by controlling the amount of added oxygen. The gasifier is operating at a pressure of 40 bar. Because of the large scale of the gasifier, the heat losses are negligible, and the gasifier is considered adiabatic.

3.4. Acid gas removal

Once the syngas out of the gasifier is cooled and water is separated, the syngas needs to be cleaned. In the hydrogen-enhanced cases, only removal of H_2S is required. Because of the high pressure of the syngas, acid gas removal based on physical solvents is considered (Selexol is chosen here). Advantages of the use of physical solvents are the pressure-swing operation without the need for extensive heating and cooling. H_2S concentration can be lowered down to 1 ppm by the Selexol cleaning system [9]. ZnO adsorption-guard beds are placed downstream of the Selexol unit to ensure the H_2S level specifications before entering the methanol reactor. By using an absorption-type process, some CO_2 is unavoidably removed as well. It is assumed that 5 % of CO_2 is removed simultaneously with the H_2S. Since MSW is richer in sulfur compared to biomass (see Table 1), it requires a more extensive acid gas removal. The Selexol off-gas which is H_2S-rich requires to be desulfurized through for example the Claus process [30].

3.5. Solid oxide electrolysis cell (SOEC)

One method to produce H_2 when low-priced renewable power is available is through water/steam electrolysis. Splitting steam through Solid Oxide Electrolysis Cell (SOEC) has several technological advantages which makes it suitable for gasification-based fuel production processes. Firstly, it has favorable thermodynamics at elevated temperatures which minimizes electrical power per unit mass of H_2 produced compared to other water electrolysis forms, such as alkaline electrolysis (AE) or proton exchange membrane (PEM) electrolysis. Moreover, by using a SOEC, the excess heat available in the gasifier outlet stream can be efficiently used to produce superheated steam required in the SOEC. The steam leaving the WHB boiler has a temperature of 700 °C which is further heated to 850 °C in a fired-heater before entering the SOEC. SOEC is emission-free production of hydrogen when clean electricity (ideally with zero-emission intensity) is available.

The simulation of the SOEC is based on adiabatic splitting steam where 80 % is converted to H_2 and O_2. SOEC is modeled with a conversion reactor and a component-splitter. Oxygen diffuses through the solid oxide membrane, producing a clean oxygen stream, leaving hydrogen and unconverted steam to exit collectively in a hydrogen-rich stream. A pure hydrogen stream is obtained by cooling down to 50 °C and condensing the water. Reheating the hydrogen stream is done through heat exchange with the hydrogen-rich stream out of the SOEC. Thermoneutral operation of SOEC at 850 °C and 40 bar is assumed. In thermoneutral operation, the cell runs adiabatically and there is no heat-transfer with the environment [9]. The energy efficiency of the electrolyzer is 83 % based on HHV of H_2 resulting in an specific electric energy need of around 33 kWh/kg_{H2}.

3.6. Natural gas pyrolysis

Natural gas pyrolysis is an emerging carbon-free hydrogen production technology [31–33]. This endothermic reaction transforms methane, in the absence of oxygen, to hydrogen and solid carbon as follows:

$$CH_4 \rightarrow C(s) + 2H_2 \quad \Delta_R H^\circ = 74.91\ \mathrm{kJ\,mol^{-1}} \tag{1}$$

Unlike SMR (steam methane reforming) where a considerable amount of CO_2 is produced, natural gas pyrolysis produces solid carbon which may have market value or can be readily sequestered. In addition, there are conditions where the cost per kg of hydrogen could be significantly less than hydrogen produced from electrolysis. However, the thermal efficiency of methane pyrolysis is 58 % because the energy of the sequestered carbon is not used [34]. The quality of the produced carbon depends on the reaction conditions and the chosen method of pyrolysis. The market price for potential carbon products can range from 400 to 2000 $/ton for carbon black to 0.1 to 600 M$/ton for carbon nanotubes [35], to only name a few products. The most prominent carbon by-product of gas-phase pyrolysis is carbon black which is made up of various forms of amorphous carbon.

In the absence of a catalyst, natural gas pyrolysis reaction occurs at temperatures above 700 °C [34], while the presence of a catalyst reduces the reaction temperature. However, to have acceptable methane conversion rates, higher temperatures are required, such as 1000 °C for thermal processes and 2000 °C for plasma routes.

Hydrogen gas purity and separation of solid carbon from reaction products without emitting CO_2 to the atmosphere are the main challenges shared among natural gas pyrolysis methods. In the plasma method of methane pyrolysis, a plasma is used to split methane, and depending on the temperature used, it is either what we refer to as “cold plasma” (temperatures below 1000 °C) or “hot plasma” (temperatures over 2000 °C). Hot plasmas provide the benefit of high conversions (near equilibrium, above 90 %) while cold plasmas in the absence of catalysts have conversions below 50 %. Challenges related to plasma methods are the requirement for a significant amount of electric power and the separation of fine carbon particles from the gas stream.

In the thermal bath approach, heat is used to split methane at temperatures between 1000 °C and 1800 °C. The molten media such as molten metals (Ti, Pb, Sn, Ga), molten metal alloys (Ni–Bi, Cu–Bi), or molten salts (KBr, NaBr, NaCl, NaF, $MnCl_2$, KCl) provide an effective heat transfer medium and can potentially act as a catalyst [36]. In literature, more studies have dealt with molten metals than molten salts [37]. The ease of separation of carbon from reaction products is facilitated due to density differences between carbon and liquid media which makes carbon aggregates to float to the surface. However, the loss of molten media in the carbon and methane conversion are engineering challenges.

The reaction temperature in moving bed reactors can be reduced to less than 1000 °C by using a metal catalyst, which is typically nickel or iron-based. Deactivation of catalysts is a major challenge due to carbon deposition on the catalyst. One way to regenerate the catalyst is to oxidize the carbon which results in the release of CO_2 into the atmosphere, contrary to the goal of producing low-carbon hydrogen. Up to now, no known commercial process produces both carbon and H_2 (fuel cell quality) as commercial products [35].

Global demand for carbon black is expected to increase to 16 Mt in 2024 [38]. Producing under 5 MtH_2/yr of hydrogen via methane pyrolysis could substitute all this demand and avoid emissions from carbon

black manufacturing [38]. With the commercialization of methane pyrolysis on a global scale, and without new markets for carbon black, there is a risk of carbon market saturation which could result in making it worthless.

In our analysis, the natural gas pyrolysis reactor is simulated by a conversion reactor in which methane is converted to H_2 and carbon black. We selected the molten media pyrolysis design from Parkinson et al. where molten metal alloy (i.e., Ni-Bi alloy) is used in a bubble column to perform catalytic thermal pyrolysis of methane at 1000 °C temperature and 35 bar natural gas pressure. The heat of the pyrolysis reaction is provided by burning 22 % of the unconverted methane. This process was chosen because the challenge of separation of the elemental carbon is facilitated using molten media. To integrate the chosen design in the process, we assume that the pyrolysis unit scales linearly in terms of mass and energy balances. While for the cost estimation, a scaling factor of 0.6 is used (explained in section 5.1). While lower pressure is better for thermodynamic equilibrium in Eq. (1), the necessity to compress H_2 for downstream use, which is a positive component of the SMR process, offsets this gain. As a result, there is a trade-off between the operating pressure and the need for downstream compression.

Natural gas is assumed to be composed of methane and enters the pyrolysis unit at 35 bar and 25 °C [32]. The generated H_2 after cooling and separation of unconverted methane is at 28 bar. It is further compressed to about 39 bar to make it suitable for injection into the downstream process. Since methane pyrolysis is an endothermic reaction, heat must be supplied to keep the operating bath temperature of 1000 °C. The pyrolysis based concept is a net generator of power, exporting 5.4 MWe to the grid for a pyrolysis unit with 100 kilotonnes per annum (kta) hydrogen production capacity [32]. By supplying all heating and electricity requirements for the pyrolysis facility by burning natural gas, the process generates approximately 2.5 $kgCO_2/kg\ H_2$ [32]. The production of CO_2 is a drawback of this process. Compared to hydrogen from SMR which generates about 10 $kgCO_2/kgH_2$ [39], the CO_2 emissions for the pyrolysis processes are approximately 25 % of that. Due to the availability of excess heat in the biomass gasification process there is potential for heat integration of a natural gas pyrolysis unit with the gasifier. This will reduce external natural gas or hydrogen firing and thus further lowers CO_2 emissions.

3.7. Methanol synthesis

Most industrial methanol production is done over Cu, Zn, and Al catalysts. Methanol is industrially produced via catalytic conversion of syngas at pressures up to 250 bar and temperatures from ~250 °C to 300 °C. In this investigation the methanol reactor operates at 80 bar and 250 °C. The methanol-synthesis reaction is exothermic; the reactor temperature is controlled by circulating boiling water as a coolant at 250 °C. The methanol reactor is simulated here assuming equilibrium is reached at reactor outlet. Methanol synthesis involves the following reactions:

$$2\,H_2 + CO \rightarrow CH_3OH \tag{2}$$

$$3\,H_2 + CO_2 \rightarrow CH_3OH + H_2O \tag{3}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{4}$$

The syngas composition at the reactor inlet is particularly important for the rate of reaction as well as product selectivity and must be such that the **M** ratio is slightly above 2:

$$\frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \tag{5}$$

In a conventional system, **M** is adjusted by using a Water Gas Shift (WGS) reactor, to shift CO and steam to CO_2 and H_2, and a subsequent CO_2 capture unit. In our hydrogen-enhanced systems, **M** is adjusted by H_2 injection.

Due to low conversion per pass in the methanol reactor, a recycle stream is required to increase the overall conversion of the syngas. To avoid the accumulation of inert components in the synthesis loop, 1 % of the reactor effluent stream is purged, which is burned in a fired heater. The raw methanol out of the reactor has water and dissolved CO, CO_2, and H_2. It is sent to the separation and purification section including a topping column and a distillation column to separate methanol to a purity of 99.5 wt%.

4. Simulation results

It is difficult to adjust the throughput of conventional methanol synthesis plants due to the high degree of mass and thermal integration in the methanol synthesis reactor. As a result, one of the constraints imposed on the design is that the methanol manufacturing plant runs at constant throughput of 48.4 tonne MeOH/hr. This translates to a BTL plant size of 418 MW_{th} and enhanced BTL and MTL sizes of 197 MW_{th} and 211 MW_{th}, respectively. The difference seen in the size of biomass and MSW plants is related to the difference in their composition and LHV.

4.1. Process performance

The simulation results for conventional BTL, enhanced BTL, and enhanced MSW to Liquid processes are shown in Table 2. Because of the low carbon efficiency of the BTL process, about twice as much biomass is required to have the same production. Carbon efficiency is defined as the proportion of the biomass carbon that ends up in Methanol product. By the addition of external hydrogen, carbon efficiency increases from 44 % to 94 %. Since RDF is richer in hydrogen and carbon compared to biomass, less feedstock is required to produce the same amount of methanol. Moreover, less hydrogen needs to be added in enhanced MSW case, decreasing the power and/or natural gas consumption. However, as a result of RDF being poorer in oxygen, it requires more oxygen from the ASU. The thermal efficiency is defined by Eq. (6):

$$\eta_{th} = \frac{\dot{m}_{\mathrm{MeOH}}\mathrm{LHV}_{\mathrm{MeOH}}}{\dot{m}_{\mathrm{b}}\mathrm{LHV}_{\mathrm{b}} + \dot{W}_{\mathrm{e}}/\eta_e} \tag{6}$$

The Lower Heating Values (LHV) are mass basis and the efficiency of thermal power to electrical power conversion (η_e) is assumed to be 50 %. While thermal efficiency as defined above gives some idea about performance of different processes, a better metric to use would be exergetic efficiency [40], since the quality of thermal and electrical power differs. By looking at methanol recycle stream composition, in the case of MSW (RDF), it is richer in nitrogen because of MSW being richer in nitrogen than biomass (see Table 1).

5. Economic analysis

5.1. Purchased equipment cost:

Equipment price data and methods to adjust equipment prices based on capacity are important in making reliable cost estimates. The purchased equipment cost can be estimated based on sizing and reference data. By knowing the purchased cost of a reference unit (C_{ref}^{unit}) and its size (A_{ref}), the size-adjusted cost (C^{unit}) is calculated by Eq. (7):

$$C^{unit} = C_{ref}^{unit} \times \left(\frac{A^{unit}}{A_{ref}}\right)^{k} \times \left(\frac{CEPCI_{current}}{CEPCI_{ref}}\right) \tag{7}$$

In order to update the capital cost from the reference year to the current values ($2020), the Chemical Engineering Plant Cost Index (CEPCI) is used. The purchased equipment costs are calculated based on the reported values in the literature. A scaling factor (k) between 0.6 and 0.8 (as detailed in Table 7) is used depending on the scalability of each piece of equipment.

Table 3
Purchased equipment cost.

	Conventional BTL	Enhanced BTL			MSW to Liquid
	BTL	BE (biomass)	BP (biomass)	BPE (biomass)	MP (MSW)
Pre-treatment	39.29	22.26	22.26	22.26	52.15
Gasification (including O_2 production)	139.76	44.99	106.40	106.40	106.06
Gas cleaning	9.35	6.27	6.27	6.27	6.27
Syngas processing (including Selexol unit)	42.56	7.42	7.42	7.42	7.42
MeOH production	19.82	19.82	19.82	19.82	19.82
Electrolyzer (including replacements)	0.00	219.54	0.00	219.54	0.00
Pyrolyzer	0.00	0.00	28.21	28.21	28.21
Power Isle	11.10	0.00	10.03	10.03	10.03
Total (M$)	261.88	320.29	200.41	419.94	229.96

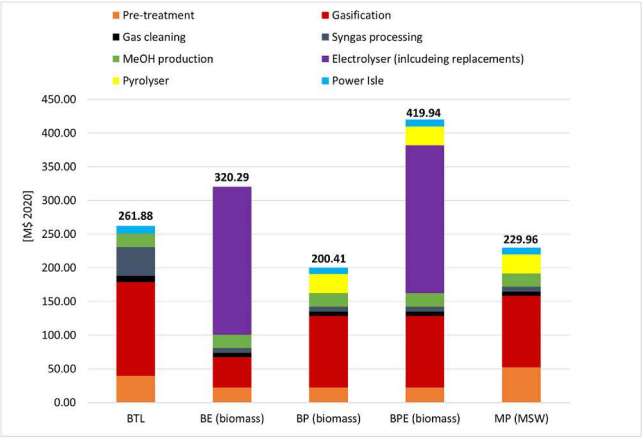

Fig. 6. Purchased Equipment cost for different cases.

The fixed capital investment (FCI) and total capital investment (TCI) for the project are estimated based on the Percentage of Delivered-Equipment Cost method [41] as shown in Eq. (8). E_i is the delivered cost of equipment i and is assumed to be 10 % of the purchased equipment cost (C^{unit} in Eq. (7)). Multipliers f_1, f_2, f_3, …, f_n are multiplying factors for piping, electrical, indirect costs, etc. The ratios used are suited for Solid-fluid processing plants [41] and are detailed in Table 8.

$$FCI_i = E_i \sum (1 + f_1 + f_2 + \cdots + f_n) \tag{8}$$

$$FCI = \sum FCI_i \tag{9}$$

Working capital (WC) is assumed to be 10 % of the total capital investment (TCI).

$$TCI = FCI + WC \tag{10}$$

Estimating by the percentage of delivered-equipment cost is commonly used for preliminary and study estimates with an expected accuracy of ±30 %. A summary of the purchased equipment cost for all five cases is given in Table 3. Since BP & MP and BE & ME processes have comparable cost estimates with the main difference being due to the added cost in the pretreatment step for MSW, only cost estimation for the MP process is provided to compare differences. Each row in Table 3 is color-coded according to its value with the largest value having dark red color. In the conventional BTL case, the plant processes twice as much biomass as used in hydrogen-enhanced cases. As a result, the pretreatment, gasification, gas cleaning, and syngas processing steps are more expensive. The use of ASU adds to the cost of gasification for BP, BPE, and MP cases. The electrolyzer unit is assumed to have a lifetime of 5 years, therefore the cost of replacements is also included.

The purchased equipment cost is shown in Fig. 6. In cases where electrolytic H_2 production is involved (BE and BPE), the electrolysis unit constitutes more than 50 % of the purchased cost, while in other cases, the gasification section forms more than half of the purchased cost estimate. The flexible BPE design has the largest equipment cost because it includes equipment that are unique to BE or BP processes, such as SOEC and pyrolysis unit.

Needless to point out in the MP process, the cost of pre-treatment equipment to produce RDF from MSW constitutes the second largest purchase equipment cost.

5.2. Levelized cost of methanol:

To investigate the economic feasibility of power and biomass to liquid process, an economic analysis is performed based on the simple and widely used Levelized Cost approach. It calculates present value of the total cost of building and operating a methanol plant over the assumed lifetime. The unit production cost of methanol is calculated by (LCOMeOH) ($/ton):

$$LCOMeOH = \frac{FCI \times CRF + C_{Opt} - C_{Byprod}}{P_{MeOH}} \tag{11}$$

Where C_{Byprod} is the annualized revenue from selling by-products, which are sulfur in all cases and carbon black in natural gas pyrolysis cases.

$$C_{Byprod} = C_{Solid\ Carbon} + C_{Sulfur} \tag{12}$$

Table 4
Main parameters for economic analysis.

Economic parameter	Value
Plant lifetime (years)	25
Interest rate (%)	10
Annual operating hours (hr/yr)	8000
Capital recovery factor (%)	11.0
Average electricity price ($/MWh)	100
Cost of biomass (5 % wet) ($/dry ton)	50
Natural Gas price ($/GJ)	5
RDF fee (5 % wet) ($/dry ton)	−30
Carbon black price ($/ton)	100
Sulfur ($/ton)	70
SOEC investment cost ($/kW)	1000

Table 5
Capital investment intensity for proposed cases with base values as in Table 4.

	Conventional BTL	Enhanced BTL			MSW to Liquid
	BTL	BE (biomass)	BP (biomass)	BPE (biomass)	MP (MSW)
Total Capital Investment (TCI) (2020 M$)	1370	1675	1048	2197	1203
Capital investment intensity ($/ton/yr)	3536	4325	2706	5671	3106

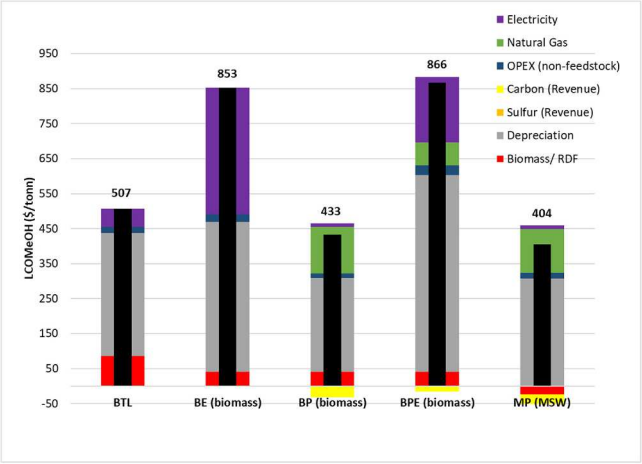

Fig. 7. The LCOMeOH costs with base values as in Table 4. The middle black columns display the net methanol production cost. Main assumptions are the installed cost of SOEC of 1000 $/kW and natural gas price of 5 $/GJ.

P_{MeOH} is the annual production rate of methanol and C_{Opt} is the annual operating cost, which is divided into feedstock and non-feedstock (biomass, natural gas, and electricity).

$$C_{Opt} = C_{Opt_feedstock} + C_{Opt_nonfeedstock} \quad (13)$$

$$C_{Opt_feedstock} = C_{Biomass} + C_{Electricity} + C_{Natural\ Gas} \quad (14)$$

$$C_{Opt_nonfeedstock} = 0.05*CAPEX \quad (15)$$

CAPEX is considered to be the overnight investment cost for building the plant and does not include costs for interest during construction or working capital [42]. The non-feedstock operating cost is declared as an annual percentage of CAPEX which is 5 %. This includes co-feeds, labor, feedstock-associated costs on-site, maintenance, and by-product disposal [42].

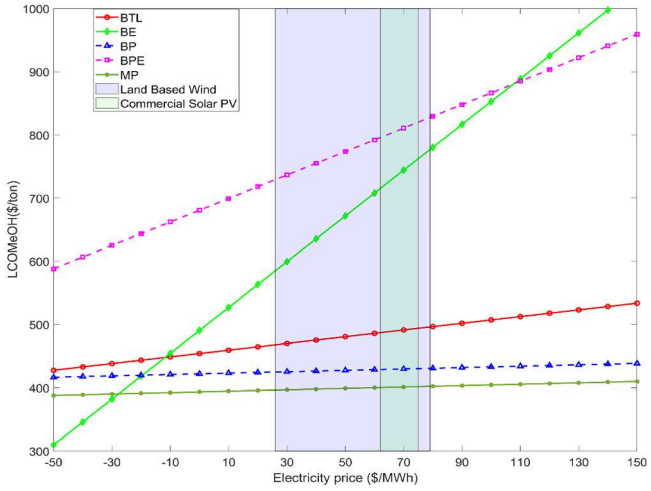

Fig. 8. Levelized cost of methanol (LCOMeOH) as a function of electricity price. The negative electricity prices are indicative of periods with curtailed renewable power. Main assumptions are the installed cost of SOEC of 1000 $/kW and natural gas price of 5 $/GJ.

In order to take into account the depreciation of the investment, Capital Recovery Factor (CRF) is used. When multiplied by the fixed capital investment (FCI), annualized depreciation cost of the invested capital is estimated:

$$CRF = \frac{i^*(i+1)^n}{(i+1)^n - 1} \quad (16)$$

where i is the interest rate and n is the plant lifetime.

The main economic parameters for evaluating Eq. (11) are shown in Table 4. We assume a value of $100 per tonne of solid carbon when sold as a feedstock for other manufacturing processes. The produced sulfur from the acid gas removal unit is assumed to have a market value of $70 per tonne. Byproducts are sources of revenue thus lowering the production costs. The base assumption for the SOEC system is an installed cost of 1000 $/kW(el) with a lifetime of **5** years [9].

The capital investment intensity ($/t/yr) is defined as the ratio of total capital investment (TCI in Eq. (10)) over the yearly methanol production (P_{MeOH}) and is shown in Table 5. The BPE has the highest capital investment intensity followed by the BE process. The BP case has the least investment intensity. The range of investment costs for a biomass-fed plant reported by IRENA and Methanol Institute [42] is assumed to be 1560–2220 $/t/yr and for MSW-based projects to be 2000–2780 $/t/yr. However, our estimates of the capital investment intensity are above the given ranges, probably due to added cost associated with the hydrogen enhancement.

The LCOMeOH with base values in Table 4 are shown in Fig. 7. As can be seen, the BPE design yields the highest production cost followed by the BE design while the MP case yields the lowest. Since in the BPE design the production cost depends on the number of operating hours in each mode (BP or BE), in this figure it is assumed that the plant operates half of the year in each mode. A closer look at the BPE design is given in section 5.5. In all cases, the depreciation cost of investment is more than 50 % of the production cost. The produced carbon in BP, BPE and MP are sources of income and thus lowers the LCOMeOH. In the MP case, the RDF fee also counts as a source of revenue and thus helps to gain an economic advantage over the BP case.

As depicted in Fig. 7, electricity price constitutes a considerable portion of the LCOMeOH in BE and BPE designs. To investigate the effect more closely, the Levelized cost of methanol as a function of electricity price for all cases is shown in Fig. 8. Irrespective of the electricity price, the MP has the lowest methanol production cost due to the "gate fee" or

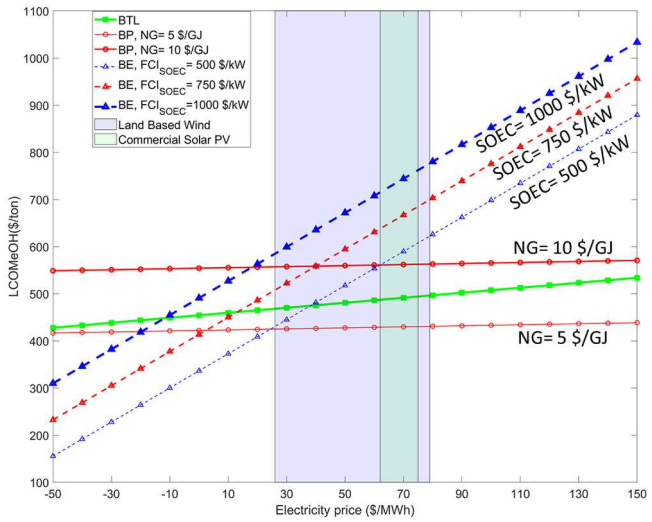

Fig. 9. Levelized cost of methanol (LCOMeOH) as a function of electricity price for BE and BP designs with two different NG prices and three different installed costs of SOEC.

Table 6
Variability ranges in the sensitivity analysis.

Variable	Base	Lower limit	Upper limit
Biomass price (5 %wet) ($/tonne)	50	10	150
Interest rate (%)	10	5	12
Plant lifetime (yr)	25	15	30
Natural gas price ($/GJ)	5	2	12
Electricity price ($/MWh)	100	0	200
Carbon black price ($/tonne)	100	20	200
RDF fee (5 %wet) ($/tonne)	−30	−100	0
Annual operating hours (hr/yr)	8000	7000	8500
Purchased equipment cost (C^{unit}) (M$)	–	−30 %	+30 %

"tipping fee" received for utilizing MSW which counts as a source of revenue. The electricity price has a strong effect on the price of methanol in the BE and BPE cases, and less in the case of BP and MP. The BPE case is assumed to run 50 % of yearly hours in BE and 50 % in BP mode, but it is more elaborated in section 5.5. If penalties for CO_2 emissions were imposed on the process emissions, the BTL would be the main loser of the game, while the rest of the processes would benefit from it. The highlighted regions in Fig. 8 depict indicative ranges of the Levelized cost of electricity for land-based wind and commercial solar photovoltaic (PV) in 2021 [43]. The results show that BP and MP processes are competitive with the BTL process, even with the current electricity prices for renewable power. Electricity price has significant impact on BE and BPE production costs. BE process would be competitive against BTL at negative electricity prices. While BTL, BP, and MP processes are not heavily dependent on electricity, the electricity price variation affects their methanol production cost, because of minor power consumption in syngas and H_2 compression, ASU, etc. In BP, BPE and MP cases, the power produced in steam turbine is enough to satisfy most of the electricity demand from the plant, including the ASU. Therefore, in BP and MP cases, the production cost is less dependent on electricity price than in BTL design.

Given a 50$/MWh electricity price and the LCOMeOH in BTL design as a reference, methanol production in the BP and MP designs is 11 % and 17 % lower, respectively, while methanol production in the BE and BPE designs is 40 % and 61 % more expensive.

To determine the impact of the SOEC cost and the natural gas price, LCOMeOH for BE and BP cases with three different installed costs of SOEC and two different natural gas prices are shown in Fig. 9. As can be seen, by decreasing the installed cost of SOEC to 500 $/kW, the cost competitiveness of BE design increases significantly. For a NG price of 10 $/GJ and an installed cost of SOEC of 500 $/kW, the breakeven electricity price for BE and BP designs would be 60 $/MW. A flexible process may benefit from changing operation mode according to feedstock prices and is discussed in section 5.5.

5.3. Local sensitivity analysis

While the main parameters used to calculate the Levelized cost of methanol (LCOMeOH) are given in Table 4, a sensitivity analysis is necessary due to the variability and uncertainty associated with the values used. By changing each variable to its upper and lower plausible limits, shown in Table 6, Tornado diagrams are generated for the proposed cases, as shown in Fig. 10 to Fig. 14.

For the BTL case (Fig. 10), the cost of biomass creates the largest variation in the Levelized cost. This is due to the low carbon efficiency of the BTL process, which results in more than 50 % of biomass carbon ending as CO_2 and thus requires twice as much biomass to produce the same amount of fuel as in other cases.

The BE case (Fig. 11) is heavily dependent on electricity price and it has a significant effect on the Levelized cost.

The sensitivity analysis for pyrolytic cases (BP and MP) are shown in Fig. 12 and Fig. 13. In both BP and MP cases, natural gas price has more pronounced effect than the electricity price. Moreover, produced carbon counts as a source of revenue and thus reduces the production cost. In the case where the carbon market is saturated, the price of carbon per ton can be as low as 20$/ton. In that case, MP and BP still hold economic advantages over the BTL process, by looking at base value in the BTL case in Fig. 10. Moreover, from the environmental aspect, large CO_2 emission reduction is gained.

In the MP case, the positive effect of RDF fee on production cost is shown in Fig. 13.

The last sensitivity analysis is for the BPE process which is shown in Fig. 14. Again, the assumption here is that the BPE plant operates half of the year in each of the BE and BP modes.

5.4. RDF fee

The economics of using MSW as feedstock is different from conventional biomass feedstocks. While biomass could cost about $50/dry ton, landfills in the US on average charge about $60/ton of MSW tipping fee [44], depending on the region. The tipping fee differs widely across the US [44]. A tipping fee or gate fee is charged to anyone who disposes of waste in a landfill. It is used to cover the operational and maintenance costs of a landfill. Tipping fees count as a source of revenue for the plant which makes the economics more favorable. Here, by varying the tipping fee of the RDF, the effect on the Levelized cost of methanol is calculated. By varying the RDF fee between −100 $/ton and 0 $/ton, the LCOMeOH increases linearly from 347 to 427 $/ton MeOH.

5.5. Flexible process

The combined BPE process (Fig. 4) is proposed with the goal of having a flexible process. It includes processing units that can change their operation mode depending on the market price of feedstocks (natural gas and electricity). During periods with high electricity price, the ASU and natural gas pyrolyzer produce the required O_2 and H_2 for the process. On the other hand, when the electricity price is low, the SOEC unit produces the O_2 and H_2 required by the process. Here one must pay attention to the point that the change in operation mode does not occur instantaneously as a result of fluctuations in electricity market price. This is because some units are not designed for fast dynamic transients. Therefore, there is a minimum number of hours that each operating mode needs to be in operation before a mode change occurs (for example 3 h). The methanol plant, however, runs at a constant rate. One important consideration for the flexible process is related to the

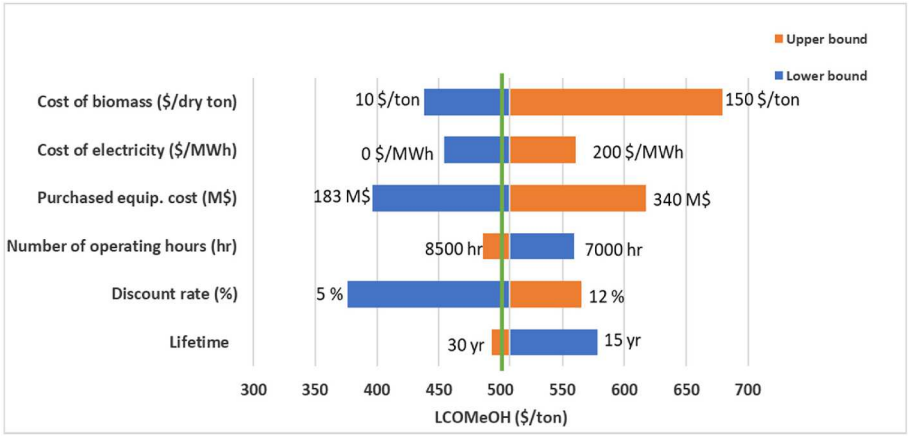

Fig. 10. Sensitivity analysis for BTL process. Solid green line indicates an average market price of 500 $/ton MeOH for the renewable methanol to compete against. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

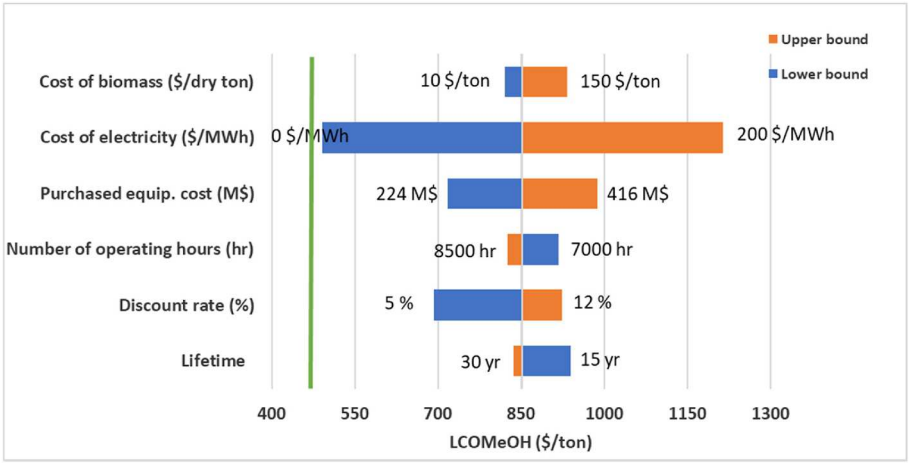

Fig. 11. Sensitivity analysis for BE process. Solid green line indicates an average market price of 500 $/ton MeOH for the renewable methanol to compete against. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

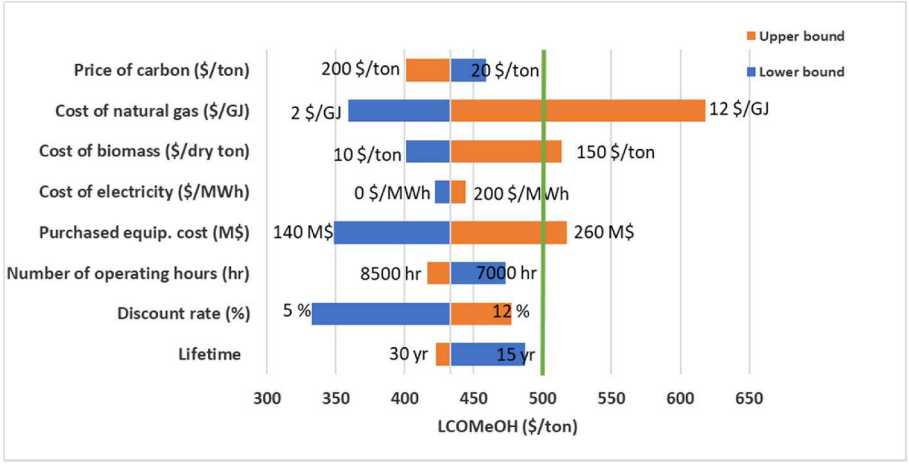

Fig. 12. Sensitivity analysis for BP process. Solid green line indicates an average market price of 500 $/ton MeOH for the renewable methanol to compete against. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

operation of units while they are in standby mode. Since both SOEC and natural gas pyrolyzer operate at elevated temperatures and both units cannot tolerate frequent heating/cooling, therefore it is necessary to keep them close to the operating temperature. This is achieved through passing hot steam through the SOEC or burning part of natural gas or hydrogen to keep the pyrolyzer at temperature. Alternatively, SOEC and pyrolyzer units can be heat-integrated with the gasifier unit. This can be done through, for example, placement of SOEC on the upper part of the

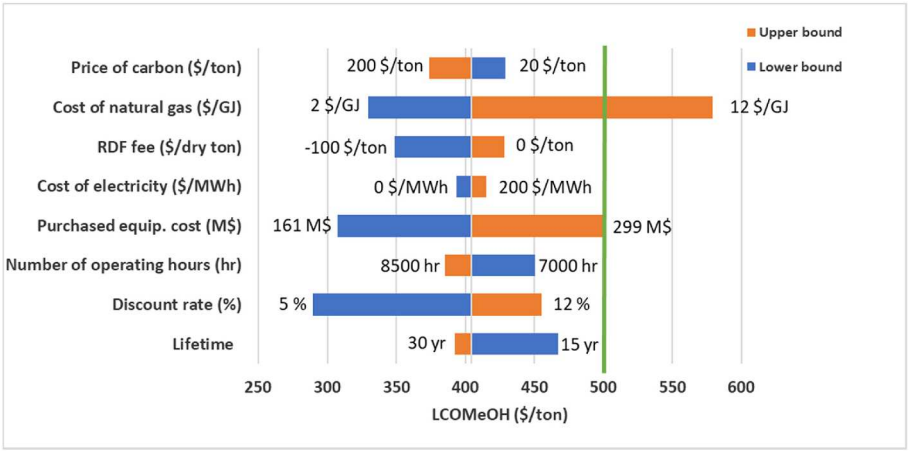

Fig. 13. Sensitivity analysis for MP process. Solid green line indicates an average market price of 500 $/ton MeOH for the renewable methanol to compete against. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

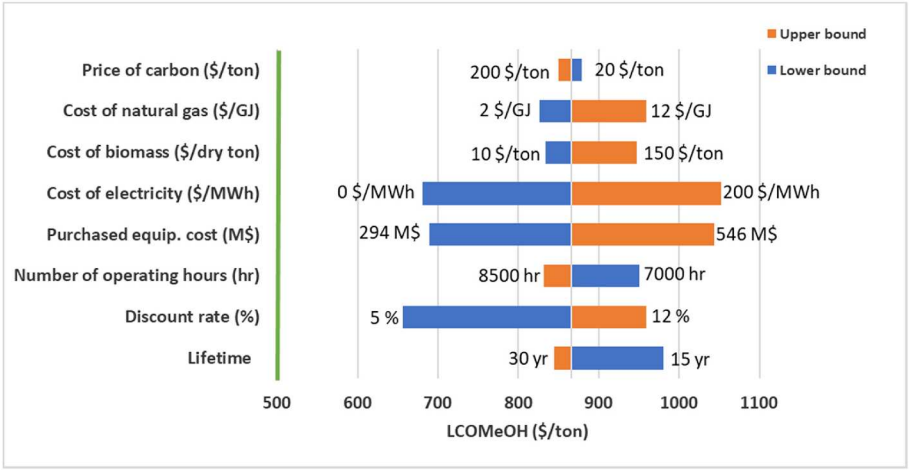

Fig. 14. Sensitivity analysis for BPE process. Solid green line indicates an average market price of 500 $/ton MeOH for the renewable methanol to compete against. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

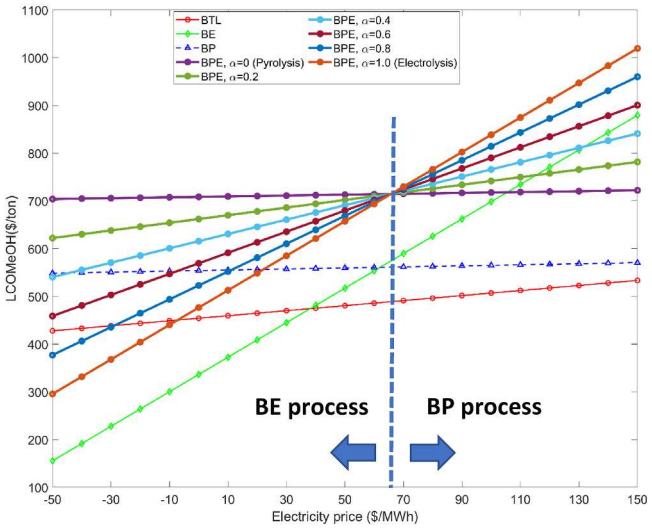

Fig. 15. The effect of α, the fraction of operational hours in BE mode, on the LCOMeOH for the combined BPE process given the assumptions of installed cost of SOEC of 500 $/kW and natural gas price of 10 $/GJ.

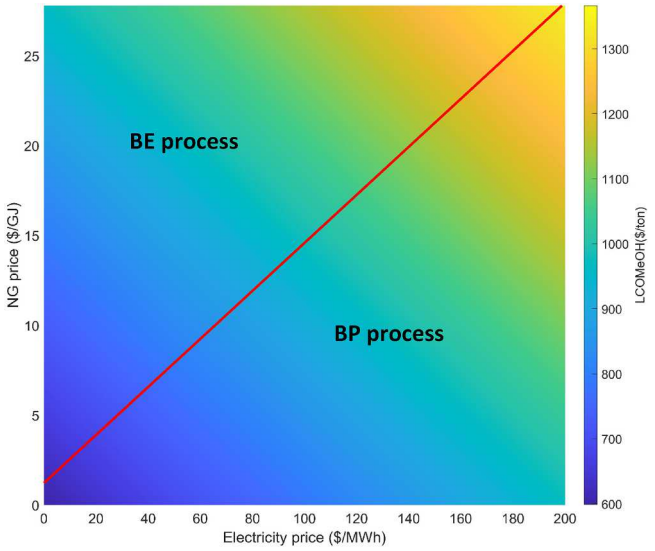

Fig. 16. Operational map of BPE process as a function of electricity and natural gas prices for installed cost of SOEC of 500 $/kW. The pivot points to change operation mode between BE and BP lie on the diagonal line.

gasifier or heating the molten media in the gasifier before entering the pyrolysis unit. These options would require more detailed simulations and analysis. Since it also takes a substantial amount of time to start the cryogenic ASU, it should be kept in "standby mode" during times when the electrolyzer is in operation. It is also assumed that the system runs in a binary fashion, either on electrolysis or in pyrolysis modes, and that each mode can by itself fulfill 100 % of the needs of the methanol plant.

The LCOMeOH in the BPE design is mainly a function of operating hours in each of BP or BE modes as well as the natural gas and electricity prices. Therefore, these variables are closely looked in this section. By taking the fraction of the total yearly operating hours in BE mode to be α and the BP mode to be (1- α), Fig. 15 is generated under the assumption of an installed cost of SOEC of 500 $/kW and a natural gas price of 10 $/GJ. In this figure, the effect of operational hours in BE mode ($\alpha = 1$) and BP mode ($\alpha = 0$) as well as combined operation ($0 < \alpha < 1$) is shown. Given these assumptions, it is interesting to note the pivot point at an electricity price of 65.7$/MWh in the figure where all lines intersect. The pivot point means that no matter which α is chosen, the operational cost is the same in all BPE cases. At this point, the cost of the electricity is almost twice that of natural gas on the same energy basis. At electricity prices above this point, the BPE process should run in BP mode and at lower electricity prices, it should run in BE mode. This mode of operation ensures lowest methanol production cost. This figure illustrates the benefit of diversifying the means of producing O_2 and H_2 in the sense that the BPE process is not bound to just one feedstock market (either natural gas or electricity) and thus can adjust based on the availability of cheapest feedstock. While natural gas and electricity prices are usually coupled and related, this coupling might be less pronounced in areas where power system is heavily dependent on renewable power, or locations where natural gas is imported to the plant from distant locations.

The electricity price at the pivot point is a function of natural gas price. Fig. 16 shows the loci of pivot point for different electricity and natural gas prices, while the color indicates the resulting LCOMeOH. At any point above the line, the BPE plant should run in BE mode and at any point below the line, where electricity is much more expensive than natural gas on energy basis, the plant should run in BP mode to ensure economic operation of the plant.

The optimal economical operation of the BPE process considering sizing of electrolyzer and pyrolyzer units and their respective capacity factors as well as natural gas and electricity prices deserve a more detailed investigation and is the subject of our future study.

6. Conclusions

This study assesses the benefits of hydrogen enhancement in biomass and MSW to liquid (methanol) conversion as well as the analysis of a new flexible process with respect to sourcing of H_2 and O_2. Three concepts (BE/ME, BP/ME, BPE/MPE) are compared in which biomass/MSW, natural gas, and renewable power are converted to methanol. The common feature of these concepts is that they rely on renewable sources and thus have low-carbon emissions. By external H_2 addition, the carbon conversion efficiency of methanol production process is roughly doubled (e.g. from 44 % to 94 %) for both biomass and MSW compared to the conventional BTL process. Two methods of H_2 production with low carbon emissions, a Solid Oxide Electrolyzer (SOEC) and a natural gas pyrolyzer, have been considered. Both hydrogen production methods benefit from the high-temperature heat available in the process (especially the gasifier exhaust stream).

The flexible BPE/MPE process is proposed to take advantage of periods with cheap feedstocks (natural gas and electricity). The flexible process has the added benefit of diversified feedstock and thus can operate economically depending on the availability of cheapest feedstocks. Aspects of the BPE/MPE process which require further investigation are the economical optimization of the flexible BPE process considering the spot natural gas and electricity prices as well as pyrolyzer and electrolyzer sizing and capacity factors. This is a subject for our future study.

Conversion of MSW (RDF) to fuel benefits from the tipping fee and thus has better economic potential compared to the use of biomass. It can also provide a substantial potential greenhouse gas reduction benefit by avoiding fugitive emissions of methane due to the decomposition of MSW organics that would otherwise be landfilled [45]. Since RDF, which is the pretreated MSW, has a composition that is similar to the biomass, it is possible to co-feed RDF and biomass. This adds to the flexibility of the process regarding the carbon source of the process.

The economic results show that BP and MP processes could be competitive with the BTL process at the scale considered, even at the current electricity prices for renewable power. Methane pyrolysis could also benefit from the existence of a market for carbon black. Cost estimates indicate that if methane pyrolysis is commercialized, it could produce the least-cost methanol among all considered cases while electrolytic hydrogen produces the most expensive methanol unless electricity prices are sufficiently low. The production cost of methanol is significantly affected by the electricity cost for the BE and BPE cases.

The illustrative natural gas pyrolysis design is not completely without CO_2 emissions (since it has an emission rate of 2.5 $kgCO_2$/kg H_2). However, these emissions are only around 25 % of the CO_2e-missions of steam methane reforming of natural gas, which is the primary present commercial method for H_2 production. Our future studies will analyze emerging means to essentially eliminate the CO_2 emissions from the natural gas pyrolysis unit through the use of renewable electricity or by burning part of H_2 produced. They will also assess the greenhouse gas emission impacts of fugitive methane emissions from the production and transportation of natural gas.

CRediT authorship contribution statement

M. Ostadi: Conceptualization, Methodology, Formal analysis, Visualization, Software, Writing – original draft, Writing – review & editing. **L. Bromberg:** Conceptualization, Methodology, Funding acquisition, Supervision, Project administration, Writing – review & editing. **D.R. Cohn:** Conceptualization, Methodology, Supervision, Writing – review & editing. **E. Gençer:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix

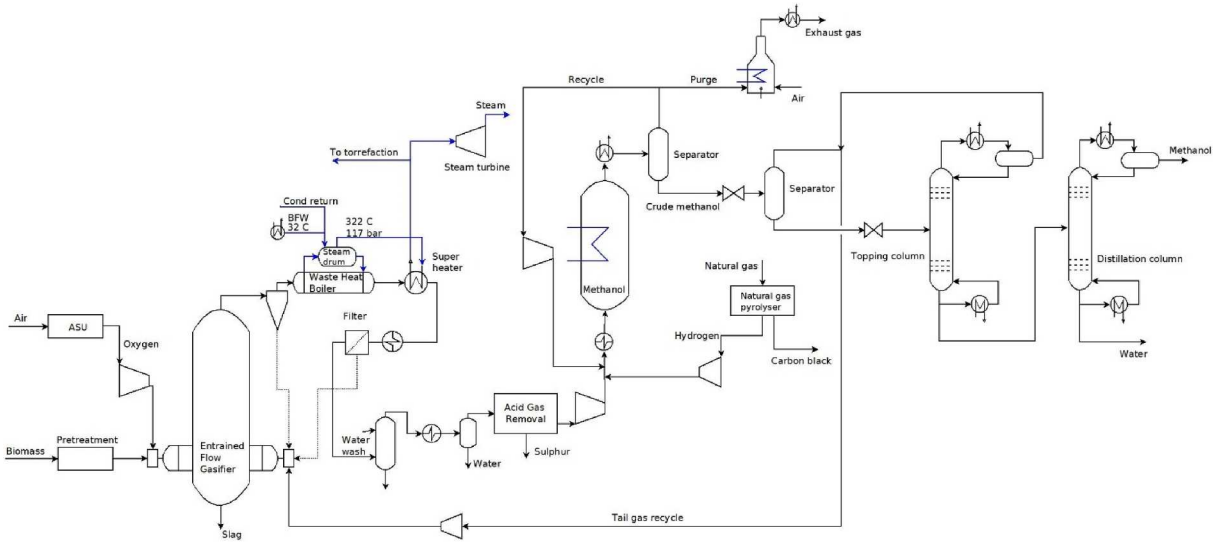

Fig. 17. Process flow diagram of BP/ MP process, where hydrogen produced from natural gas pyrolysis is added.

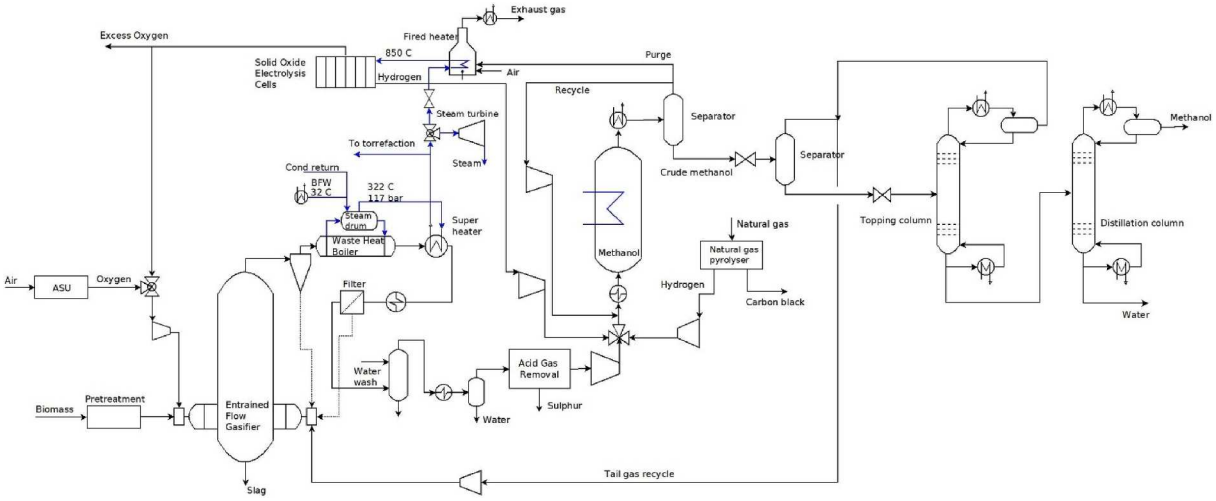

Fig. 18. Process flow diagram of BPE/MPE process, where hydrogen is produced from natural gas pyrolysis and/or Electrolysis.

Table 7
Purchase equipment cost.

Unit	Base cost	Scale factor	Base scale	Unit	Year	Reference
Pre-treatment						
Conveyers	0.41	0.8	33.5	wet tonne/h	2002	[24]
Grinding	0.48	0.6	33.5	wet tonne/h	2002	[24]
Storage	1.16	0.65	33.5	wet tonne/h	2002	[24]
Dryer	8.5	0.8	33.5	wet tonne/h	2002	[24]
Iron removal	0.43	0.7	33.5	wet tonne/h	2002	[24]
Feeding system	0.48	1	33.5	wet tonne/h	2002	[24]
Gasification system						
Entrained Flow (EF) gasifier (gasifier, Lock hopper, water quench)	63.4	0.65	2000	dry ton/d	2007	[46]
Air separation unit (99.5 % O_2)	27.9	0.75	576	tonne O_2/d	2002	[24]
Oxygen compressor	18.1	0.85	13.2	MWe	2002	[24]
Gas cleaning						
Tar cracker	3.6	0.7	34.2	m^3/s gas	2002	[24]
High-temperature heat exchanger	8.1	0.6	138.1	MWth	2002	[24]
Dry gas cleaning	35.8	1	74.1	m^3/s gas	2002	[24]
Guard beds (ZnO + active C)	0.024	1	8	m^3NTP/s gas	2002	[24]
Syngas processing						
Compressor	12.9	0.85	13.2	MWe	2002	[24]
Shift reactor	12.2	0.65	8819	kmol CO + H_2/h	2002	[24]
Selexol	63	0.7	9909	kmol CO_2/h	2002	[24]
Methanol production						
Gas phase methanol	7	0.6	87.5	tonne MeOH/h	2001	[3]

(*continued on next page*)

Table 7 (*continued*)

Unit	Base cost	Scale factor	Base scale	Unit	Year	Reference
Refining	15.1	0.7	87.5	tonne MeOH/h	2001	[3]
SOEC						
SOEC ($1000/kW)	1000			kWe	2018	[9]
Pyrolysis						
Pyrolysis unit	40.8	0.6	100	ktonne per year	2016	[32]
H_2 compressor (in Euro)	5.7	0.67	10	MWe	2010	[8]
Power Island						
Steam turbine + steam system	5.9	0.7	10.3	MWe	2002	[24]
MSW Pre-treatment						
MSW handling and RDF facility	143.49	0.77	45.2	RDF kg/s	2015	[47]

Table 8
Ratio factors for estimating capital investment items based on delivered-equipment cost. The ratios used are suitable for "solid–fluid processing plant" [41].

Direct Costs	Fraction of delivered equipment cost
Purchased equipment installation	0.39
Instrumentation & Controls (installed)	0.26
Piping (installed)	0.31
Electrical systems (installed)	0.10
Buildings (including services)	0.29
Yard improvements	0.12
Service facilities (installed)	0.55
Total direct costs	**2.02**
Indirect Costs	
Engineering and supervision	0.32
Construction expenses	0.34
Legal expenses	0.04
Contractor's fee	0.19
Contingency	0.37
Total indirect costs	**1.26**

References

[1] "Lazard's Levelized Cost of Energy analysis — version 14.0," 2020.
[2] Bromberg L, Cheng WK, "Options for sustainable and / or energy-secure transportation," no. 4000096701, p. 78, 2010.
[3] Hamelinck CN, Faaij APC. Future prospects for production of methanol and hydrogen from biomass. J Power Sources 2002;111(1):1–22. https://doi.org/10.1016/S0378-7753(02)00220-3.
[4] Tock L, Gassner M, Maréchal F. Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. Biomass Bioenergy 2010;34(12):1838–54. https://doi.org/10.1016/j.biombioe.2010.07.018.
[5] Hannula I, Kurkela E, Liquid transportation fuels via large-scale fluidised-bed gasification of lignocellulosic biomass. VTT Technical Research Centre of Finland, 2013. doi: VTT Technology 91.
[6] Holmgren KM, Berntsson T, Andersson E, Rydberg T. System aspects of biomass gasification with methanol synthesis – process concepts and energy analysis. Energy 2012;45(1):817–28. https://doi.org/10.1016/j.energy.2012.07.009.
[7] Clausen LR. Maximizing biofuel production in a thermochemical biorefinery by adding electrolytic hydrogen and by integrating torrefaction with entrained flow gasification. Energy 2015;85:94–104. https://doi.org/10.1016/j.energy.2015.03.089.
[8] Hannula I. Co-production of synthetic fuels and district heat from biomass residues, carbon dioxide and electricity: Performance and cost analysis. Biomass Bioenergy 2015;74:26–46. https://doi.org/10.1016/j.biombioe.2015.01.006.
[9] Hillestad M, et al. Improving carbon efficiency and profitability of the biomass to liquid process with hydrogen from renewable power. Fuel 2018;234. https://doi.org/10.1016/j.fuel.2018.08.004.
[10] Butera G, Methanol production integrating biomass thermochemical conversion and solid oxide cells. 2020.
[11] Salladini A, Borgognga A, Agostini E, Annesini MC, Iaquaniello G. Power to liquid through waste as a carbon source: a technical and economic assessment. Int J Hydrogen Energy 2020;45(46):24467–76. https://doi.org/10.1016/j.ijhydene.2020.06.232.
[12] Iaquaniello G, Centi G, Salladini A, Palo E, Perathoner S, Spadaccini L. Waste-to-methanol: process and economics assessment. Bioresour Technol 2017;243:611–9. https://doi.org/10.1016/j.biortech.2017.06.172.
[13] Valkenburg C, Walton C, Thompson B, Gerber M, Jones S, Stevens D. Municipal solid waste (MSW) to liquid fuels synthesis, volume 1: availability of feedstock and technology. Using Municipal Solid Waste for Fuel 2011;1(December):1–41.
[14] Jones S, Zhu Y, Valkenburg C. Municipal solid waste (MSW) to liquid fuels synthesis, volume 2: A techno-economic evaluation of the production of mixed alcohols. Using Municipal Solid Waste for Fuel 2011;2(April):43–140.
[15] Borgogna A, Salladini A, Spadacini L, Pitrelli A, Annesini MC, Iaquaniello G. Methanol production from refuse derived fuel: influence of feedstock composition on process yield through gasification analysis. J Clean Prod 2019;235:1080–9. https://doi.org/10.1016/j.jclepro.2019.06.185.
[16] Seidl LG, Lee RP, Keller F, Meyer B. Chemical utilization of carbonaceous waste and lignite – a case study of sustainable olefin production in Germany. DGMK Tagungsbericht 2019;2019(3):101–15.
[17] Böhme C, "Innovations for a climate-friendly chemical production," BASF press conference, Ludwigshafen, 2019.
[18] "https://monolith-corp.com/".
[19] "https://www.czero.energy/".
[20] "https://www.ekonapower.com/".
[21] Poluzzi A, et al., "Flexible Power & Biomass-to-Methanol plants: design optimization and economic viability of the electrolysis integration," Fuel, vol. In press, no. PA, p. 122113, 2022, doi: 10.1016/j.fuel.2021.122113.
[22] Steinberg M. The Carnol process for CO2 mitigation. Energy Convers Manag 1996;37(6–8):843–8.
[23] Ott J, et al., "Methanol," Ullmann's Encyclopedia of Industrial Chemistry, 2012.
[24] Hamelinck CN, Faaij APC, den Uil H, Boerrigter H. Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential. Energy 2004;29(11):1743–71. https://doi.org/10.1016/j.energy.2004.01.002.
[25] Ostadi M, Hillestad M. Enriched Air or Pure Oxygen as Oxidant for Gas-to-Liquid Process with Microchannel Reactors. Chem Eng Technol 2017;40(10):pp. https://doi.org/10.1002/ceat.201700269.
[26] Waldheim L, IEA BIOENERGY, and WALDHEIM CONSULTING, Gasification of waste for energy carriers. A review, vol. Task 33. 2018.
[27] Burnham AK, "Estimating the Heat of Formation of Foodstuffs and Biomass," pp. 1–11, 2010.
[28] Ostadi M, Rytter E, Hillestad M. Boosting carbon efficiency of the biomass to liquid process with hydrogen from power: The effect of H2/CO ratio to the Fischer-Tropsch reactors on the production and power consumption. Biomass Bioenergy 2019;127(June):105282. https://doi.org/10.1016/j.biombioe.2019.105282.
[29] Hameed Z, et al., "Gasification of municipal solid waste blends with biomass for energy production and resources recovery: Current status, hybrid technologies and innovative prospects," Renewable and Sustainable Energy Reviews, vol. 136, no. March 2020, p. 110375, 2021, doi: 10.1016/j.rser.2020.110375.

[30] Mokhatab S, Poe WA, "Sulfur Recovery and Handling," Handbook of Natural Gas Transmission and Processing, pp. 291–316, Jan. 2012, doi: 10.1016/B978-0-12-386914-2.00008-X.
[31] Parkinson B, Matthews JW, McConnaughy TB, Upham DC, McFarland EW. Techno-economic analysis of methane pyrolysis in molten metals: decarbonizing natural gas. Chem Eng Technol 2017;40(6):1022–30. https://doi.org/10.1002/ceat.201600414.
[32] Parkinson B, et al. Hydrogen production using methane: Techno-economics of decarbonizing fuels and chemicals. Int J Hydrogen Energy 2018;43(5):2540–55. https://doi.org/10.1016/j.ijhydene.2017.12.081.
[33] Upham DC, et al., "Catalytic molten metals for the direct conversion of methane to hydrogen and separable carbon," Science (1979), vol. 358, no. 6365, pp. 917–921, 2017, doi: 10.1126/science.aao5023.
[34] Steinberg M. Fossil fuel decarbonization technology for mitigating global warming. Int J Hydrogen Energy 1999;24(8):771–7. https://doi.org/10.1016/S0360-3199(98)00128-1.
[35] Dagle RA, Dagle V, Bearden MD, Holladay JD, Krause TR, Ahmed S, "An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products," (No. PNNL-26726; ANL-17/11). Pacific Northwest National Lab.(PNNL), Richland, WA (United States); Argonne National Lab.(ANL), Argonne, IL (United States)., p. 65, 2017.
[36] Sánchez-Bastardo N, Schlögl R, Ruland H. Methane pyrolysis for zero-emission hydrogen production: a potential bridge technology from fossil fuels to a renewable and sustainable hydrogen economy. Ind Eng Chem Res 2021;60(32):11855–81. https://doi.org/10.1021/acs.iecr.1c01679.
[37] Palmer C, Tarazkar M, Gordon MJ, Metiu H, McFarland EW. Methane pyrolysis in low-cost, alkali-halide molten salts at high temperatures. Sustain Energy Fuels 2021;5(23):6107–23. https://doi.org/10.1039/d1se01408k.
[38] IEA, "The Future of Hydrogen Seizing today's opportunities," 2019.
[39] International Energy Agency, "The Future of Hydrogen - Seizing today's opportunities," *The Future of Hydrogen*, no. June, 2019, doi: 10.1787/1e0514c4-en.
[40] Ostadi M, Austbø B, Hillestad M. Exergy analysis of a process converting power and biomass to a liquid fuel. Chem Eng Trans 2019;76:205–10. https://doi.org/10.3303/CET1976035.
[41] Peters MS, Timmerhaus KD, West RE. Plant design and economics for chemical engineers. 5th ed. Boston: McGraw-Hill; 2003.
[42] Irena and methanol institute. Innovation outlook: Renewable mini-grids. Abu Dhabi: International Renewable Energy Agency; 2021.
[43] National Renewable Energy Laboratory, "2021 Annual Technology Baseline (ATB) Cost and Performance Data for Electricity Generation Technologies," 2021, doi: 10.25984/1807473.
[44] "https://www.wasteinfo.com/news/wbj20210728.htm." (Retrieved Jan.10.2022).
[45] Zhao H, "Methane Emissions from Landfills," MSc. Thesis, Columbia University, 2019.
[46] Zhang H, Wang L, Pérez-Fortes M, Van herle J, Maréchal F, Desideri U, Techno-economic optimization of biomass-to-methanol with solid-oxide electrolyzer, Appl Energy, vol. 258, no. May 2019, p. 114071, 2020, doi: 10.1016/j.apenergy.2019.114071.
[47] Niziolek AM, Onel O, Floudas CA. Municipal solid waste to liquid transportation fuels, olefins, and aromatics: process synthesis and deterministic global optimization. Comput Chem Eng 2017;102:169–87. https://doi.org/10.1016/j.compchemeng.2016.07.024.