



Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts



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HIGHLIGHTS

- We model 3 biomass to biochar and methanol concepts to compare their profitability.
- Pyrolysis is more sensitive to biomass costs and the selling price of biochar.
- Biochar selling prices above \$220/t will yield breakeven for some pyrolysis concepts.
- The internal rates of return for all the concepts lie between 10.1% and 14.2%.

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ABSTRACT

Methanol is one of the fuels that are an alternative to petroleum-based liquid transport fuels. This paper assesses the feasibility of co-production of methanol and biochar from thermal treatment of pine in a two-stage process; pyrolysis or gasification to produce biochar and volatiles, and the processing of the volatiles to produce methanol using process data for large-scale conversions based on natural gas. Three concepts were studied: (i) slow pyrolysis at 300 °C; (ii) slow pyrolysis at 450 °C; and (iii) gasification at 800 °C, all of them followed by processing of the volatiles into syngas and the conversion of the syngas into methanol. Gasification was able to generate methanol at or below current (2012) prices of methanol produced from fossil fuel (\$422/t) from a plant size of 100 t/h upwards. Pyrolysis is not competitive without valuing the biochar as a product. Considering both biochar and methanol as marketable products improves the viability of slow pyrolysis concepts. Their profitability is sensitive to the biochar selling price between, with a break-even at a biochar price of about \$220/t for the pyrolysis at 300 °C and about \$280/t for pyrolysis at 450 °C.

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1. Introduction

Renewable transportation fuels, including liquid fuels produced from biomass [1–4], are under investigation as alternatives to petroleum. Thermal pathways for conversion of biomass to liquid fuels typically also produce a solid carbon-rich residue ('char' or 'biochar' if applied to soil). The greater the quantity of biochar that is produced, the more of the heating value of the original biomass feedstock remains in this solid residue. Processes that aim to convert biomass to liquid fuel typically seek to minimize biochar production to maximize liquid fuel production. Thus, the most commonly proposed routes from biomass to liquid fuels are via gasification and fast pyrolysis [5]. However, it has been shown that

biochar, if it is added to agricultural soils, has significant potential to simultaneously improve soil fertility [6], while reducing atmospheric greenhouse gas concentrations by sequestering carbon [7–9]. Co-production of biochar with bioenergy can provide a greater climate-change mitigation impact than biofuel production alone [8,10], whilst also providing the co-benefit of increased agricultural productivity on poor soils [6].

Producer gas (sometimes called pyrolysis gas), which is a mixture of mainly CH₄, light hydrocarbons, CO, H₂, H₂O, and volatile organic compounds, evolves from the pyrolysis of biomass. Conversion of producer gas into liquid fuel is a promising route that offers a high-value product [11–13]. The producer gas is typically converted into syngas (a CO- and H₂-rich mixture) as an intermediate product, and then converted to ethanol, methanol, or Fischer–Tropsch hydrocarbons, via biological or catalytic processes. Among these pathways to liquid fuels, we focus on catalytic processes as having the lowest uncertainty in production costs and methanol as having the simplest production process.

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Catalytic methanol production from syngas is a well-established process, with multiple commercial technologies developed by different companies.¹ However, the syngas for these processes is mainly produced by steam reforming of natural gas. Therefore, uncertainties remain in regard to the level of clean up of biomass-derived syngas that is needed to prevent metal catalyst poisoning. Other studies [4,14,15] have evaluated the techno-economics of biomass gasification for the synthesis of methanol and other liquid fuels. As is the case with methanol production from fossil fuels, production costs using biomass gasification show considerable economies of scale [4]. Methanol production costs have been found to decrease from \$83.70/GJ to \$30.40/GJ when plant size increases from 10 to 2000 MW (thermal), for a South African setting [4]; the larger plant's production costs are about 1.5 higher than the 2012 US prices of methanol from natural gas, with an average of \$422/t (\$18.59/GJ) [16] (taken as an average of 2010–2012 prices to account for the methanol price volatility).

Even though biochar may improve sustainability of biofuel production through its positive effects on soil health [9], a market and consequently a value of biochar has not yet been generally established [17]. Typically, the production of a biochar co-product increases the cost of biofuel production as it decreases the biofuel yield [17,18]. Brown et al. [18] have compared slow pyrolysis producing biochar and fuel gas versus fast pyrolysis producing bio-oil and biochar. They conclude that a process that primarily produces biochar is unlikely to be profitable, due to the low value of biochar assumed in their study. The magnitude of such tradeoffs for catalytic methanol production and the sensitivity to the as-yet-unknown market value of biochar has not previously been established.

2. Material and methods

2.1. Biomass conversion technologies

A simplified layout of the biomass to biochar and methanol conversion process (Fig. 1) shows the components included in modeling the energy and mass balances. Fig. 1a starts with slow

pyrolysis, while Fig. 1b starts with gasification; after these initial steps the producer gases are processed through tar cracking, cleaning, compression, optional water gas shift and catalytic methanol production, all of which processes are described below.

Three different thermochemical conversion concepts were studied. (1) Py300: pyrolysis at 300 °C to maximize the biochar yield. This concept gives the highest biochar yield (80% of the biomass' carbon) and the least syngas. The resulting low syngas volume implies smaller syngas conditioning component sizes and lower equipment costs per unit of biomass feedstock (although not per unit of methanol produced). (2) Py450: pyrolysis at 450 °C, typical of slow pyrolysis units [19,20]. This concept converts about 45% of the carbon to biochar, and is within the temperature range that produces optimal biochar quality [21] and (3) Gas800: gasification at 800 °C for maximum syngas yield, for comparison with pyrolysis. This concept leaves only about 15% of the carbon in biochar by mass.

2.1.1. Syngas production

The syngas for the process is produced in two stages: pyrolysis and tar cracking. The gaseous and volatile products from pyrolysis at the temperatures considered consist of a complex mixture of volatilized tars and other condensable organic compounds, C1–C3 hydrocarbons, CO₂, H₂O, some CO, and small amounts of H₂. In contrast, the methanol synthesis stage requires a syngas that consists primarily of CO and H₂. Therefore, a tar-cracking unit was included in the process to both convert the volatile products to a syngas rich in CO and H₂. The heating conditions in these two stages determine the composition and yield of the syngas.

Syngas composition and yield for the pyrolysis scenarios (Py300 and Py450) are obtained from experimental pyrolysis data for pine from Enders [22] summarized in the [Supplementary Information](#). The overall C, H and O composition of the combined gaseous and volatile product mixture (and thus, of the final syngas composition) is similar for pyrolysis temperatures above 350 °C, but volatiles' yield increases with temperature. Composition and yield for the gasification scenario were calculated from elemental C, H and

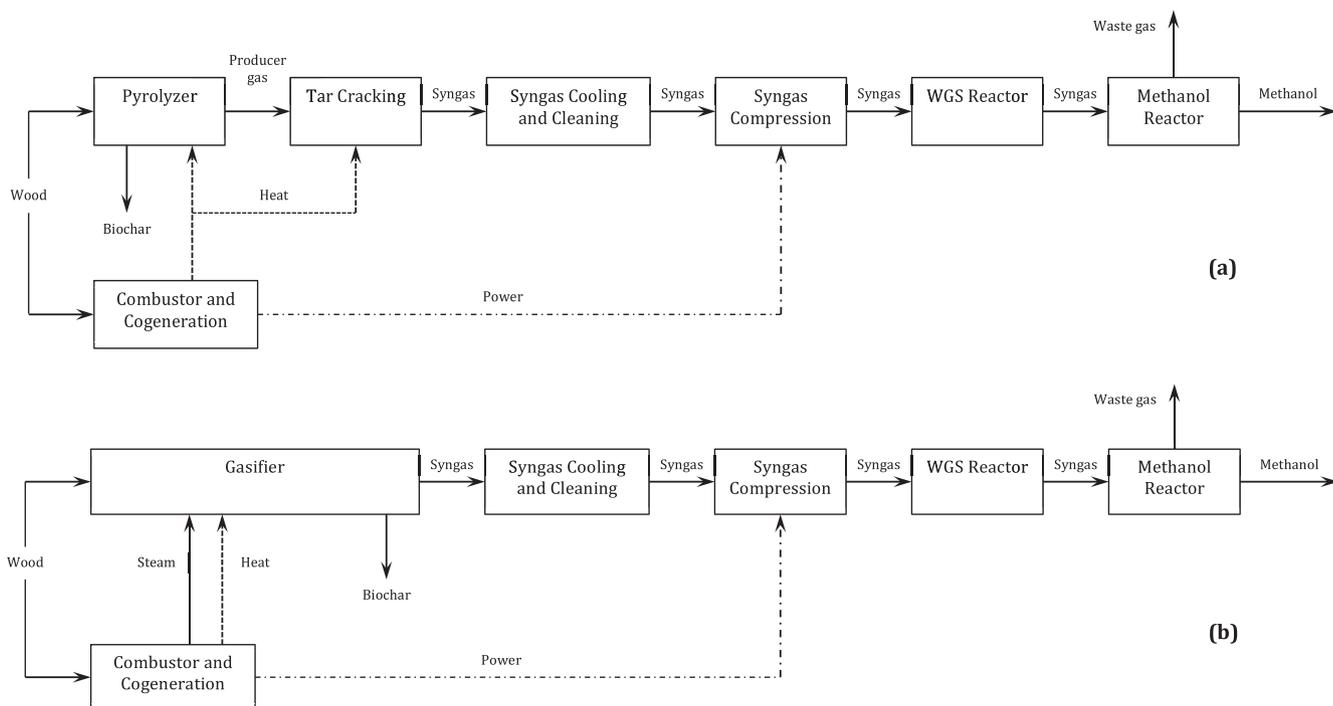


Fig. 1. Schematic layout of a biomass to methanol and biochar plant.

O composition of pine and steam (in proportions typical of steam blown gasification) brought to equilibrium at 800 °C, with a C (graphite) yield of 7% by mass which represents the biochar yield for gasification. The equilibrium composition was calculated using Chemical Equilibrium with Applications (CEA) software [23].

Tar cracking was modeled using chemical equilibrium at 800 °C, also using CEA. The tar cracking temperature of 800 °C was intended to limit the formation of polyaromatic hydrocarbon (PAH) pollutants in the syngas, production of which is negligible at temperatures up to 800 °C but increases dramatically above this temperature [24]. Tar-cracking temperatures below 800 °C also entail lower conversion. Boroson et al. [25] studied homogeneous tar cracking of wood pyrolysis vapors at the temperature range of 500–800 °C and reported conversions of 5–88%, respectively.

The syngas composition and flow rate were used to size equipment for the remaining stages, namely: syngas cooling, conditioning, water gas-shift reactor, and methanol synthesis. The same components were assumed to be present, regardless of the scale of the plant. The amount of tars remaining after the tar-cracking stage was estimated at 40 g/kg of dry biomass using data for gasification systems [26].

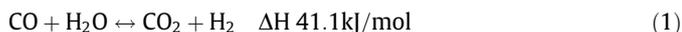
2.1.2. Heat generation for thermochemical conversion

Heat and power for the process are provided through combustion of biomass to provide steam and power; the biomass fuel for this process was modeled as a separate stream (see Fig. 1) from the biomass converted into syngas and methanol.

2.1.3. Syngas processing

The hot syngas requires cleaning and cooling before it can be converted to methanol. The syngas from the tar-cracker or gasification unit is cooled from 800 °C to 300 °C in a shell-and-tube heat exchanger and then passes through a condensing scrubber, which removes moisture, particulates and the remaining tars, while cooling the syngas to 90 °C. The syngas then passes through a compressor to reach 50 bar and 250 °C. The syngas then passes into a water–gas shift reactor to increase the hydrogen content of the syngas.

The optimal H₂:CO ratio of the syngas required for the methanol synthesis is approximately 2:1 (molar) [1]. A water gas shift (WGS) unit can be used to manipulate the H₂:CO ratio (Eq. (1)). The reaction is exothermic and proceeds nearly to completion at low temperatures. Catalysts for this process are active at temperatures as low as 200 °C [27].

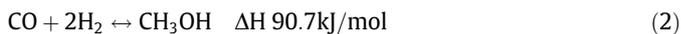


The H₂/CO molar ratio for the volatiles at equilibrium for pyrolysis at 300 °C with tar-cracking is about 1.9, which is close to the methanol synthesis stoichiometry of 2. Thus a water–gas shift reactor is not needed for Py300. In contrast, for Py450 and Gas800, the syngas H₂:CO molar ratios were about 1.1:1, necessitating a water–gas shift reactor.

2.1.4. Methanol generation

The last stage in the process is the synthesis of methanol from CO and H₂, which was modeled based on similar reactors [9] to be a single pass process with a 90% conversion of the CO, which is a conservative value compared to the 99% predicted from an equilibrium calculation. This leaves 10% of the CO unused, which, because it is mixed with CO₂, is considered a waste stream. Methanol is produced from syngas by the hydrogenation of carbon oxides over suitable Cu/ZnO-based catalysts (which are susceptible to poisoning and thus need highly conditioned syngas) at 220–300 °C and 50–100 bar (Eq. (2)) [27]. The operating temperature selected for the methanol synthesis was 255 °C rising to 260 °C from the

exothermicity of the reaction, and no heat recovery from the exiting waste gas was assumed.



2.2. Economic analysis

The methanol production costs were calculated by dividing the total annual cost by the amount of methanol produced. The total annual costs consist of annualized capital costs (calculated assuming an interest rate of 10%); operating and maintenance costs (together, estimated to be 4% of the capital cost, as in Hamelinck [2]); and biomass feedstock cost.

The total installed costs were calculated by a factored estimation from the literature [1,2], based on the major equipment required for syngas processing, including conveying, chipping, storage, feeding, pyrolysis or gasification, tar-cracking, syngas cooling, syngas cleaning and compression, water–gas reaction and methanol synthesis. All capital costs are in 2012 dollars with the equipment cost inflation calculated using the Chemical Engineering Plant Cost Index (CEPCI) for the two periods [28,29]. Hamelinck [1] gives the uncertainty range of such estimates as up to ±30%. The unit investments depend on the size of the components, by scaling from data in the literature [1,2]. The overall installed cost of the plants for Py300, Py450 and Gas800 scenarios was calculated from using a total project investment factor of 4 as a rounded-off figure between the Lang factor of 3.6 [30] for a mixed fluids–solids processing plant given by Sinnott (1998), Jones and Zhu (2009) figure of 3.73 [15] and Peters and Timmerhaus' (1980) figure of 4.22 [31]. Table 1 summarizes the main assumptions used in the calculations as well as the baseline figures and their assumed variability.

3. Results and discussion

3.1. Mass and energy balance

Yield of volatiles increases with temperature, as does the CO and H₂ fraction of the volatiles (Table 2). The yield of methanol

Table 1
Sensitivity analysis inputs.

	Low	Baseline	High
Plant size (t/h)	50	100	150
Biomass cost (\$/t)	40	50	100
Methanol selling price (\$/t)	379	422	465
Biochar selling price (\$/t)	100	250	500
Interest rate (%)	5	10	15
Total project investment factor	3	4	5
Plant operations			
Project lifetime (years)	25		
Operating time (hours/year)	8000		
Operational costs	4% of total installed investment		

Table 2
Syngas composition (mass frac), yields of biochar and methanol for the concepts.

	Py300	Py450	Gas800
<i>Syngas composition (mass frac)</i>			
CO	0.29	0.71	0.81
CO ₂	0.39	0.16	0.08
CH ₄	0.00	0.004	0.01
H ₂	0.04	0.06	0.06
H ₂ O	0.28	0.07	0.03
Biochar yield (kg/kg _{dry biomass})	0.58	0.26	0.07
Methanol yield (kg/kg _{dry biomass})	0.10	0.25	0.31

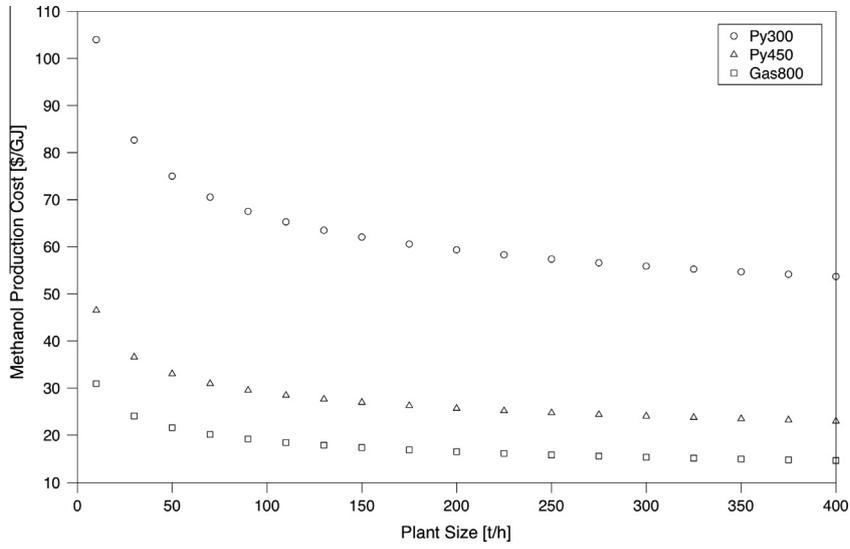


Fig. 2. Methanol production costs in relation to plant size.

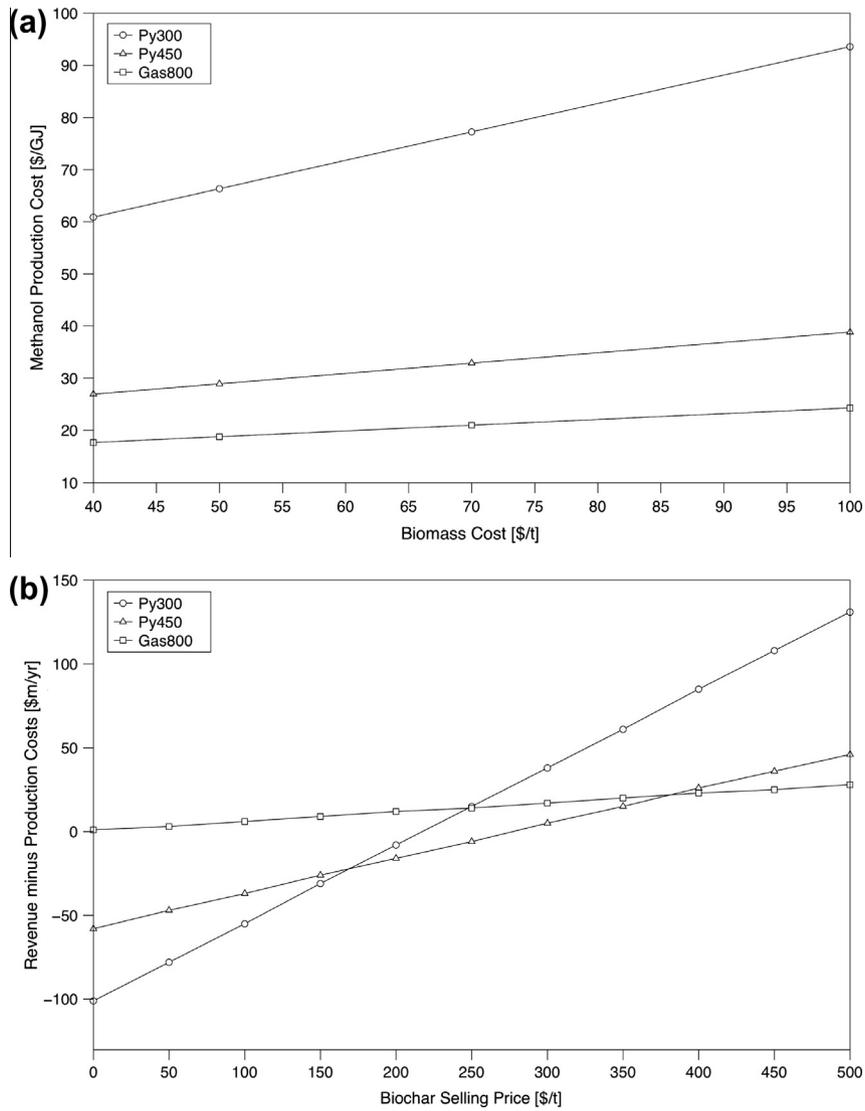


Fig. 3. (a) Methanol production costs in relation to biomass cost and (b) Profitability in relation to biochar cost, for a plant size of 100 t/h.

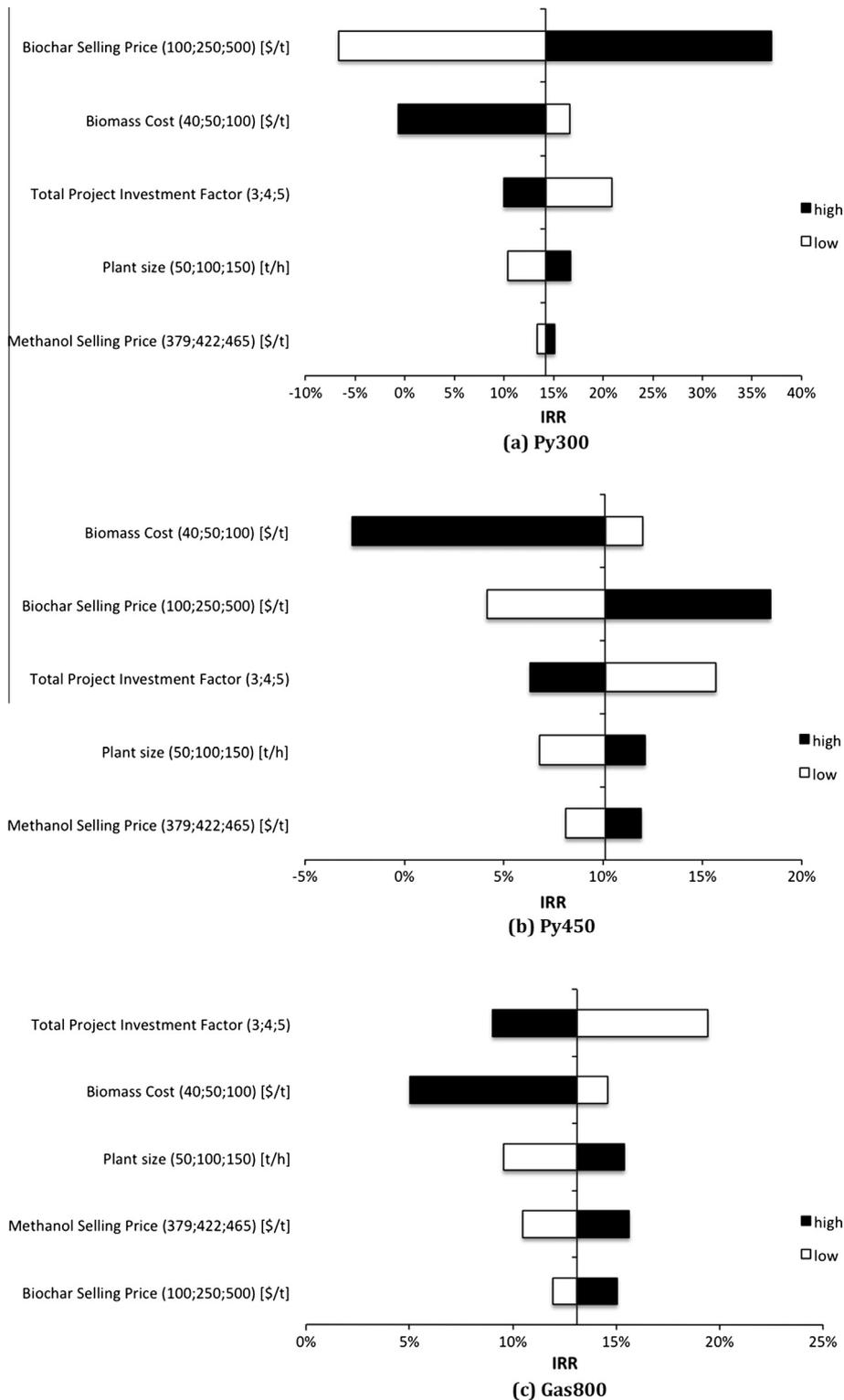


Fig. 4. Sensitivity analysis for a plant size of 100 t/h for (a) Py300 (b) Py450 and (c) Gas800.

(which is dependent on the amount of CO and H₂ available) increases with an increase in the temperatures of the pyrolysis and gasification due to these conditions favoring the CO and H₂ production. Biochar yield, on the other hand, falls with increasing pyrolysis temperature, and is significantly lower for gasification. The biochar yields for the concepts were 58% for Py300, 26% for Py450 and 7% for Gas800.

The energy efficiencies calculated for the biomass to methanol conversion concepts, defined here as the combustion enthalpy in the methanol divided by the combustion enthalpy in the original biomass feedstock (including additional biomass used to provide process heat and power), was 15% for Py300, 42% for Py450 and 57% for Gas800, with yields of methanol (liters) per ton of dry biomass of 130 l/t, 310 l/t, and 390 l/t, respectively.

3.2. Methanol production costs excluding biochar value

Fig. 2 presents the methanol production costs for the three concepts over the plant size range between 10 t/h and 400 t/h. The current methanol commodity price is about \$422/t (\$18.59/GJ) on the world market [16]. Fig. 2 shows that, when the value of the biochar is not taken into account, then Gas800 would require a plant size of above 100 t/h to be economically viable (i.e. to produce methanol at a cost that is lower than the current bulk price generated from natural gas), while neither of the pyrolysis concepts would be competitive. Py300, which had the highest biofuel production cost (Fig. 2) because it yielded the lowest quantity of methanol per operating cost of the plant, will produce methanol only at costs above \$50/GJ for the entire range of plant sizes considered, if the value of the biochar is neglected. Methanol production costs for Py450 are above \$30/GJ for plant sizes below 100 t/h.

A higher cost of biomass increases the methanol production cost (Fig. 3a). For a plant of 100 t/h, only gasification would be competitive compared to US methanol prices, and only if the biomass costs are below \$50/t. Biomass costs are often the most uncertain and volatile costs in biofuel production [32]. Biomass can be produced in the U.S. in the cost range of \$40/t to \$60/t [32]. Amigun et al. (2010) data [4] examined biomethanol from non-woody biomass gasification for a wide range of plant sizes ranging from 400 t/h to 2 t/h and calculated methanol production costs of \$30.40/GJ to \$83.70/GJ, respectively. These data suggest that the resulting methanol production costs of \$18.79/GJ to \$30.93/GJ for a size range of 400–10 t/h in this study would need to be adapted for plants to be located in a different setting.

3.3. Economic analysis of a methanol-biochar system

If biochar as well as methanol is considered as a saleable product, then the profitability of the plant depends on the selling price of biochar. Assuming a biomass throughput of 100 t/h and a methanol selling price of \$422/t (\$18.59/GJ), varying the biochar price between \$0/t and \$500/t (which currently is the upper limit for biochar for soil amendment in the US [33]), profitability is very sensitive to the biochar price for Py300 and Py450 but less sensitive for Gas800 (Fig. 3b). The viability of the biochar-methanol system for a 100 t/h plant requires that the biochar would have a market price of at least \$280/t for the Py450 whereas for Py300 the minimum is \$220/t. The capital costs for the 100 t/h concepts are \$525 m, \$685 m and \$775 m for Py300, Py450 and Gas800 respectively. The gasification concept capital cost of \$775 m is comparable to \$606 m [13] (2010 figure) for biomass to liquid fuel via gasification.

The key variables identified to have significant impact on the profitability of the methanol-biochar system were the cost of the biomass, the value of the products (methanol and biochar) and the capital costs as represented by the plant size and the total project investment factor. Fig. 4 shows the impact of varying the baseline figures on the viability of the concepts as indicated by the internal rate of return (IRR). The IRR can be compared to prevailing rates of return on the market, with negative values representing the loss of part of the initial investment. The baseline for the concepts was a plant size of 100 t/h, a total project investment factor of 4, a methanol price of \$422/t (\$18.59/GJ) and a biochar price of \$250/t with the IRRs being 14.2% for Py300, 10.1% for Py450 and 13.1% for Gas800. Biochar selling price and biomass cost have the highest impact on profitability for the pyrolysis concepts (Fig. 4a and b). The biochar selling price of \$100/t to \$500/t varied the IRR from –6.7% to 37% for Py300, from 4.1% to 18.4% for Py450. The total project investment factor and biomass cost have the highest impact for the gasification concept (Fig. 4c). The total baseline value of the total

project investment factor is close to the value estimated for similar plants based on the type of process [30,31] as well as that used for biomass to methanol and other liquid fuels via gasification [15]. Uncertainty in the value for the total project investment factor leads to considerable uncertainties in the IRR for all the concepts with IRR highs of 15.7% to 20.8% and lows of 6.3–10%. For a plant that aims to produce biochar and methanol, the biochar revenues have to make up for the methanol output that is forgone by leaving more of the carbon in the biochar compared to gasification. For the baseline conditions, the revenue from the biochar-methanol stream is about 70% from biochar (30% from methanol) for Py300, 30% from biochar (70% from methanol) for Py450 and 10% from biochar (and 90% from methanol) for Gas800. These numbers are based on the same selling value of the biochar produced from the different-temperature treatment, which will not be the case in practice. The baseline biochar selling value of \$250/t is unlikely to be achieved for Py300 biochar (which is a low-temperature biochar and potentially not as valuable as Py450 biochar). For Py450 the biochar break-even selling value is \$280/t and Py300 biochar has a break-even selling value of \$220/t. The biochar from gasification (Gas800) is likely of more limited agronomic value due to its low organic C content as well as the possible presence of PAHs or dioxins [34].

4. Conclusions

The profitability of three biochar-methanol concepts were investigated, with pyrolysis at 300 °C to maximize biochar quantity, pyrolysis at 450 °C to maximize biochar quality and gasification at 800 °C to maximize syngas output. Capital costs for a plant size of 100 t/h are estimated at \$525 m for Py300, \$685 m for Py450 and \$775 m for Gas800. When the biochar is not valued, the pyrolysis concepts Py300 and Py450 do not yield enough quantity of syngas to make the methanol prices competitive at current US selling price. The baseline IRRs for Py300, Py450 and Gas800 are 14.2%, 10.1% and 13.1%. The baseline break-even selling price for the biochar for the concepts is \$220/t, \$280/t and \$0/t for the Py300, Py450 and Gas800 respectively. The baseline break-even selling price for the methanol for the concepts is \$263/t (\$11.60/GJ), \$444/t (\$19.55/GJ) and \$387/t (\$17.07/GJ) for Py300, Py450 and Gas800 respectively. The break-even selling price of methanol for Gas800 when the biochar is not valued (to relate to other biomass to liquid fuels via gasification) is \$18.51/GJ compared to \$15.73/GJ [14] for a biomass to MTG via gasification.

Pyrolysis at 300 °C due to its high yield of biochar and the low output of methanol is the most sensitive to biomass costs (IRR from 16.6% to –0.6%) and the price at which biochar can be sold (IRR from –6.7% to 37%). Pyrolysis at 450 °C is most sensitive to biomass costs (IRR from 12% to –2.6%) and the price at which biochar can be sold (IRR from 4.1% to 18.4%). Gasification at 800 °C is most sensitive towards total project investment factor (IRR from 19.4% to 9%) and biomass costs (IRR from 14.6% to 5%).

Biochar may help in decreasing biofuel costs when local soil conditions and cropping systems justify a market and sufficiently high price for the biochar (>\$220/t). Future research should investigate opportunities for distributed and smaller-scale conversion facilities using biomass rather than fossil fuel by providing direct process based data from pilot facilities.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2013.08.053>.

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