

Self-Sustainable Bio-methanol & Bio-char Coproduction from 2nd Generation Biomass Gasification

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Methanol is an important intermediate in the synthesis of different chemicals. It is mainly produced by reforming of natural gas in centralized facilities with productive capacities on the order of 10⁹ tons per day. Production of methanol from biomass suffers from the cost and logistics of the transportation of biomass and it has not yet matured into commercial scale. The techno-economic feasibility of the co-production of bio-methanol and bio-char is assessed through detailed computer simulations using process simulator Aspen HYSYS[®] together with the gasification simulator GASDS. This work further elaborates the previous results on the bio-methanol production process, presenting particularities and updates on previously reported values. The production model is seen to be valid, with payback times that go from 3 to 6 years according to the capacity of the plant (100 to 1000 kt of biomass per year). Self-sustainability is possible but a 50/50 mix of producing and buying electricity yields the most economic choice.

1. Introduction

In a previous work by these authors a superstructure was introduced in order to elect potential biomass-to-chemicals processes while presenting a preliminary description of bio-methanol and bio-char coproduction (Amaral et al., 2016). This work further elaborates the coproduction process, presenting particularities and updates on previously reported values. The techno-economic feasibility of the process is assessed through detailed computer simulations using process simulator Aspen HYSYS[®] together with the gasification simulator GASDS. Methanol is an important intermediate in the synthesis of different chemicals (Bozzano and Manenti, 2016). It is mainly produced by reforming of natural gas and in centralized facilities with productive capacities on the order of 10⁹ tons per day (Dahl et al., 2014). Production of methanol from biomass gasification profits from bio-char coproduction but suffers with the cost and logistics of the transportation of biomass. It has not yet matured into commercial scale; production over distributed facilities is likely to follow from these limitations. The results on the following sections point on capacities of 100 to 1000 tons per day in these facilities.

2. Biomass

One of the objectives of this work is to aggregate value on second generation biomass, since it is a residual, low-valued and abundant material (Fatih Demirbas, 2009). *Arundo donax*, a high productivity energy crop was chosen as representative of potential second generation biomass for the process. Its main features were determined with the works of (Corno et al., 2014) and (Wang, 2013) and are summarized in Table 1 below. These properties are important in determining gasification output. Based on the capacity of current and on-going bio-methanol projects, biomass provisions were estimated at 500 kt per year (IEA-ETSAP and IRENA, 2013).

Table 1: Summary of *Arundo donax* properties.

| | | | | |
|----------------------|--------------|-----------------------|------------------|-------|
| Main components | Cellulose | Hemicellulose | Lignin | Ashes |
| Mass % of dry weight | 40.0 | 28.9 | 26.7 | 4.4 |
| Property | Moisture [%] | Particle diameter [m] | Bed porosity [%] | |
| Value | 6.9 | 0.0366 | 76 | |

3. Process Scheme

Figure 1 below is an Aspen HYSYS® flowsheet which represents the methanol production process. The first step of the process is biomass gasification, which produces a solid residue, bio-char (not shown) and producer gas, i.e., a gas rich in H₂, CO, CO₂, H₂O but which also contains CH₄, dust and tars. The producer gas follows into the gas conditioning operations (steps 2 to 5) which remove all of the components which do not participate in methanol synthesis; the gas stream is then almost entirely composed of H₂ and CO and is called syngas. Steps 6 and 7 are the synthesis and purification (distillation) of methanol while in step 8 heat and electricity are generated by burning syngas, bio-char or both. In Table 2 the steps are summarized according to their order and function while in Table 3 the composition and properties of the streams exiting each operation are presented.

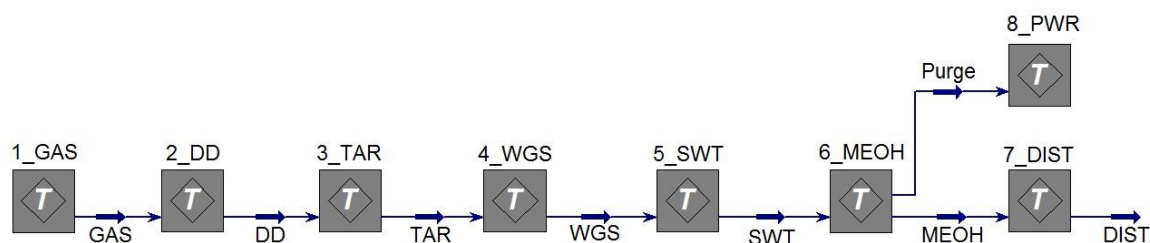


Figure 1: Aspen HYSYS® flowsheet showing the biomass conversion process.

Table 2: Summary of the processing steps according to their order and function.

| Operation # | Name | Function |
|-------------|--------------------------|--|
| 1 | Gasification | Partially oxidizes biomass to generate producer gas and bio-char |
| 2 | Dedusting | Removes particulates |
| 3 | Tar reforming | Tar and CH ₄ steam reforming |
| 4 | Water-gas-shift reaction | Adjusts the H ₂ /CO ratio of the gas stream |
| 5 | Sweetening | Removes CO ₂ and H ₂ S from the gas |
| 6 | MeOH synthesis | Produces MeOH from syngas |
| 7 | Distillation | Removes impurities (mainly water) from the product |
| 8 | Power generation | Generates heat and electricity |

Table 3: Streams properties: composition (kg/h), temperature (°C) and pressure (kPa).

| Operation # | Component mass flow [kg/h] | | | | | | | | T (°C) | P (kPa) |
|-------------|------------------------------|------|-----------------|----------------|-----------------|-------|------------------|-------|--------|---------|
| | Soot | Tar | CH ₄ | H ₂ | CO ₂ | CO | H ₂ O | MeOH | | |
| 1 | 350 | 8638 | 2463 | 1226 | 19790 | 23572 | 18968 | 17 | 814 | 101 |
| 2 | 0 | 8638 | 2463 | 1226 | 19790 | 23572 | 18968 | 17 | 814 | 88 |
| 3 | 0 | 0 | 45 | 3301 | 25392 | 38817 | 11340 | 0 | 800 | 88 |
| 4 | 0 | 0 | 45 | 4063 | 42008 | 28230 | 553 | 0 | 50 | 1800 |
| 5 | 0 | 0 | 45 | 4058 | 2292 | 28200 | 452 | 0 | 54 | 1740 |
| 6 | 0 | 0 | 15 | 6 | 2183 | 81 | 249 | 30769 | 40 | 7300 |
| 7 | 0 | 0 | 0 | 0 | 188 | 0 | 5 | 30551 | 40 | 101 |

3.1 Gasification

Gasification output was calculated with gasification simulator GASDS, which is presented elsewhere (Cabianca et al., 2016). Biomass gasification was performed on a counter-current, updraft gasifier, in the presence of steam and pure oxygen at atmospheric pressure. After a few trials a configuration was chosen for

the gasification operation in such a way that steam and oxygen consumption were kept to a minimum. Operational parameters are shown on Table 4.

Table 4: Summary of operating conditions of the gasifier.

| Operational parameter | Unit | Value |
|--|----------|-------|
| Gasifier pressure | [kPa] | 101 |
| Temperature of gases entering the gasifier | [°C] | 227 |
| Gasifier height | [m] | 20 |
| Gasifier diameter | [m] | 2 |
| Biomass input | [kt/y] | 500 |
| Oxygen input | [kt/y] | 100 |
| Steam input | [kt/y] | 50 |
| Temperature of gases exiting the gasifier | [°C] | 814 |
| Bio-char output | [kt/y] | 54 |
| Producer gas output | [kt/y] | 601 |

These operating conditions maintain exit gases at a temperature close to 800 °C and 1 atm, which is important for the following reasons:

- Avoid alkali melting / slagging problems;
- Avoid excessive tar formation in the gasification operation;
- Avoid excessive oxidation of the biomass, leading to high amounts of CO₂ on the gas;
- Avoid tar condensation on the dedusting section;
- Providing the reforming section with input that is already at the reforming temperature (800 °C);
- Providing the reforming section with input that is already rich in steam;
- Avoid having the reforming section with a too high CO₂ partial pressure.

The effects of CO₂ partial pressure in the reforming section will be explained in section 3.4.

3.2 Dedusting

Dedusting was dimensioned by considering that 5% of the mass of the bio-char produced was carried away as fines - 0.1 mm in diameter with a density of 170 kg/m³. In the process simulator, the gas was first passed through a cyclone (which collected 95% of fines) and the rest was removed through filtering. The filtering unit was not dimensioned in Aspen HYSYS[®], where instead, a simple separator was used. To size the filter unit, total gas volume was considered in order to calculate the required number of filter cartridges. A 5 cm/s filtering velocity was considered with negligible pressure drop. No heat loss was considered in the process and gas temperature remained unchanged.

3.3 Tar reforming

Tar steam reforming was modelled by considering the two hot catalytic beds presented in the work of (Pinto et al., 2014). Gas flows through a first “guard” bed filled with calcined dolomite (the main constituent of which is calcium-magnesium oxide, CaMgO₂) and a second bed filled with a common alumina-supported nickel-oxide catalyst; both of the beds are kept at 800 °C. The first bed (by having a more resilient, cheap catalyst) is responsible for destroying part of the tars and reduces the probability of coke deposition in the second bed. If gasification was conducted under pressure, the partial pressure of carbon dioxide in the reforming section might be too high, which could cause catalyst deactivation on the guard bed according to Eq(1):



Tar and methane steam reforming are endothermic reactions presented on Eq(2) and Eq(3), respectively:



It can be seen that Eq(3) is Eq(2) with $(x, y, z) = (1, 4, 0)$. In Aspen HYSYS[®] the reforming reactions were modelled by considering the chemical equilibrium of the gas at 800 °C. Since the software finds difficulty in solving directly the equilibrium with the high number of components arising from gasification a three step strategy was used. Figure 2 presents it in detail: the gas coming from the dedusting section is first brought to equilibrium at 50 °C (GBR1 block), which releases heat (stream h_GBR1). At this temperature, the only

components present are CH_4 , CO_2 , H_2O and a tiny amount of H_2 . The products coming out of the first reactor pass through 'cutter' elements, which change the number of components considered from 45 to 9: H_2 , CO , CO_2 , H_2O , CH_4 , MeOH , O_2 , N_2 and C . The resulting streams are then recombined in a second block (GBR2) which brings the mixture to equilibrium at $800\text{ }^\circ\text{C}$, consuming heat (stream h_GBR2). This whole procedure is equivalent to considering that, at equilibrium conditions, no tar species are present. Since the reforming reactions are endothermic, oxygen should be inserted into the system for it to operate at $800\text{ }^\circ\text{C}$. To calculate how much oxygen is consumed in the reforming step, in a third block (GBR3) the mixture is brought to chemical equilibrium at $800\text{ }^\circ\text{C}$ while inserting oxygen and removing heat. The quantity of heat removed equals the heat provided in the second block minus the heat released in the first block, as shown in Eq(4). This quantity is also important in calculating the cost of investment (COI) of this section.

$$h_{GBR3} = h_{GBR2} - h_{GBR1} \quad (4)$$

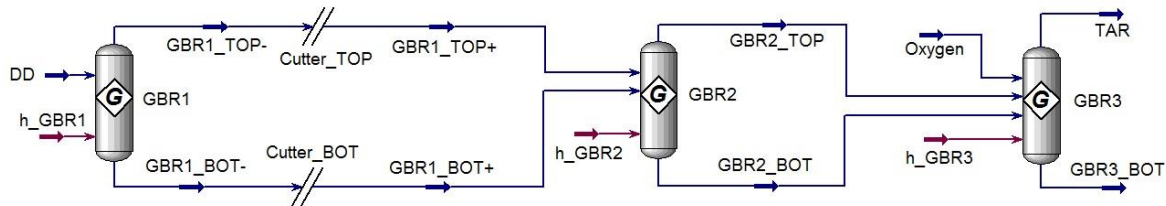


Figure 2: The tar reforming section with a three step equilibrium strategy.

3.4 Water-gas shift reaction (WGSR)

The water-gas shift reaction (WGSR) adjusts the H_2/CO molar ratio according to Eq(5):



The WGSR is exothermic and is catalyzed by an iron-supported chromium oxide catalyst. Kinetics and catalyst properties were determined from the works of (Turton et al., 2012). The target H_2/CO molar ratio is 2, as it will be seen from the methanol synthesis stoichiometry, section 3.6. Figure 3 gives further details on the simulation: gas received from the previous section is pressurized at 2000 kPa in a series of compressors with inter-stage water removal. The exit temperature of each compressor is limited to $150\text{ }^\circ\text{C}$ because of compressor oil decomposition/volatilization. High pressure steam (8000 kPa , $500\text{ }^\circ\text{C}$) is added to the gas stream so that the molar ratio of H_2O to reacted CO is 2:1. The gas mixture is brought to the temperature of $360\text{ }^\circ\text{C}$ and reaction follows in a water-cooled, multi-tubular plug-flow reactor (MTPFR). Afterwards, the gas is cooled down to $50\text{ }^\circ\text{C}$ and most of the water is condensed and removed.

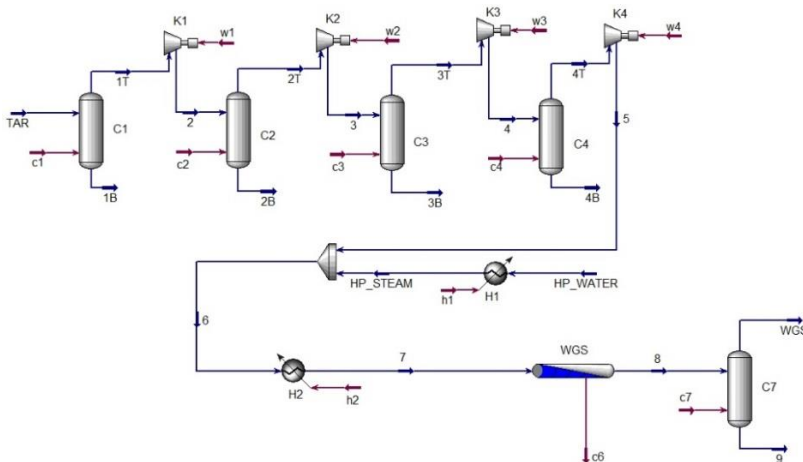


Figure 3: Detail of the WGSR section in Aspen HYSYS®.

3.5 Sweetening

In the sweetening step the gas stream is stripped of CO_2 and H_2S by absorption in two 40-stage column with an amine/water solution (4:6 amine to water mass ratio) at 70% CO_2 loading (CO_2/amine molar ratio). The amine used was N-methyl-diethanolamine (MDEA). The first objective of this step is to protect the methanol

synthesis catalyst from the poisoning effect of H₂S, even though its concentration in the producer gas is approximately 100 ppmv (Simell et al., 2014). For the high-temperature steps (reforming and WGSR) such levels are acceptable but for methanol synthesis a value bigger than 100 ppbv would cause catalyst poisoning (Levalley et al., 2014). For a gas stream containing 100 ppmv H₂S, the aforementioned configuration satisfactorily reduces H₂S levels below 100 ppbv. The second function of this step is to remove CO₂. Its removal has two positive effects on the process, both which related to the next step, methanol synthesis; the first effect is to block the reverse WGSR (which is also promoted by the synthesis catalyst); the second effect is to reduce costs associated with gas compression.

3.6 Methanol synthesis and distillation

Methanol synthesis is an exothermic reaction, catalyzed by an alumina-supported copper-zinc oxide catalyst. The reaction takes place at 7500 kPa and 250 °C in a water-cooled MTPFR and is presented on Eq(6). Kinetics were determined from the work of (Graaf et al., 1988) while physical properties were determined from the work of (Turton et al., 2012). In this step, gas received from the previous section is pressurized and enters the reaction loop. After reaction, the stream is cooled down to 40 °C; methanol and water condense, separate from unreacted syngas and follow for the distillation section. In the distillation section a 30-stage distillation column produces 99.5 % mass purity methanol and recovers 99% of the methanol produced. Part of the unreacted syngas is recirculated while the other fraction is purged and used for heat and electricity production.



3.7 Power generation and heat exchanger network

The power generation section is comprised of two circuits; in the first one, heat is generated in a furnace, fed with bio-char, unreacted syngas or both, and air; in the second one, electricity is generated in a steam turbine. After deciding how much heat and power will be produced in this section, a Pinch analysis of the whole simulation model enables (1) calculating utility requirements and (2) dimensioning the heat exchanger network.

4. Economic analysis

The economic analysis was performed by calculating the cost of investment (COI) of each section and the net operational income (NOI). COI was estimated with the procedures presented by (Turton et al., 2012) while catalyst and filter cartridges prices were determined from suppliers at the Alibaba.com website (Alibaba Group, 2017). Three cases were considered and are presented on Table 5 with their respective payback times (PBT).

Table 5: Payback times of three different bio-char / bio-methanol concepts.

| Case # | Electricity produced [%] | Syngas burned [%] | Bio-char burned [%] | PBT [y] |
|--------|----------------------------|---------------------|-----------------------|-----------|
| 1 | 50 | 5 | 0 | 3.5 |
| 2 | 100 | 22 | 0 | 3.8 |
| 3 | 100 | 5 | 73 | 4.3 |

Table 6: Summary of COI and NOI for the first case.

| Operation | COI [Mi EUR] | Consumable/Product | NOI [Mi EUR/y] |
|------------------------|----------------|----------------------|------------------|
| Gasification | 61 | Biomass | -22 |
| Dedusting | 1 | Oxygen | -21 |
| Tar reforming | 8 | Filter cartridges | -1 |
| WGSR | 40 | Catalyst (Reforming) | -2 |
| Sweetening | 2 | Catalyst (WGS) | -3 |
| MeOH synthesis | 12 | Catalyst (Synthesis) | -2 |
| Distillation | 1 | Cooling water | -1 |
| Power generation | 8 | Electricity | -11 |
| Heat exchanger network | 13 | Bio-char | 32 |
| TOTAL | 147 | Bio-MeOH | 91 |
| | | TOTAL | 60 |

No hot utilities were used in any of the cases. With current electricity prices (0.125 € / kWh) there is advantage in buying it over burning syngas or bio-char. Moreover, since bio-char costs more than methanol (600 and 370

€/ t, respectively), burning the former is less rentable. Table 6 individuate items in the COI and NOI for the first case, which performs best (information on Table 3 also refers to this case). A power-law rule can be used to scale COI as a function of the capacity of the plant (Turton et al., 2012). The results of such approach are presented on Table 7 below. It is easy to justify a bigger investment in this case: not only the NOI is bigger but also the PBT is smaller (its value being approximated from the ratio between COI and NOI +1 year of construction). It is then clear that the smaller the capacity of the design the less economically competitive it is.

Table 7: Payback times of three different bio-char / bio-methanol concepts.

| Biomass input [kt/y] | COI [Mi EUR] | NOI [Mi EUR/y] | PBT [y] |
|------------------------|----------------|------------------|-----------|
| 100 | 56 | 12 | 5.7 |
| 500 | 147 | 60 | 3.5 |
| 1000 | 223 | 119 | 2.9 |

5. Conclusions

A model for co-producing bio-char and methanol from biomass gasification was presented. Its techno-economic feasibility was attested, showing its capacity to substitute current oil-based technologies. For every 100 kg of biomass processed, approximately 50 kg of bio-methanol and 10 kg of bio-char are produced. Self-sustainability with respect to external sources of energy is possible but it is not the most economic choice. A mix of 50/50 produced and bought electricity yields the optimal choice.

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