Revamping of the Mantova Chemical District as Short-chain Lignocellulosic Biorefinery

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The Mantova Chemical District is a Site of National (and European) Interest (SIN). It comprises an oil refinery specialized in gasoline owned by Mol and Ies societies, a petrochemical plant (olefins) owned by Eni Versalis, an air separation unit and a reformer plant owned by Sapio and a series of industries working in the area of chipboard. Nowadays the oil refinery is off and the industrial network is deeply suffering from it; authorities at all levels (town, province, region, and ministry) are moving fast to convert the old facility into a biorefinery.

This paper illustrates the studies and partial results of the funded project BioMAN for the conversion of the old refinery into a lignocellulosic biorefinery. A process framework was proposed for the establishment of an integrated biorefinery based on stablished and emerging technologies. In future works, a further elaboration of such scheme will allow determining optimal operating conditions through optimization algorithms.

A preliminary economical assessment of methanol production showed potential for revenue production: accumulated net income was 61 mi € in five years. Methanol production was 50 kt per year; the yearly amount of biomass required, approximately 160 kt, is in agreement with current reports of local availability.

1. Introduction: The Mantova Chemical District

The Mantova Chemical District is a Site of National (and European) Interest (SIN). It comprises an oil refinery specialized in gasoline owned by Mol and Ies societies, a petrochemical plant (olefins) owned by Eni Versalis, an air separation unit and a reformer plant owned by Sapio and a series of industries working in the area of chipboard. Mantova's SIN uses about 150 kt/y of methanol to produce formaldehyde, the main component for furnishing (about the 70% of the products of IKEA™ are based on the Mantova SIN). Nowadays the oil refinery is off and the industrial network is deeply suffering from it; authorities at all levels (town, province, region, and ministry) are moving fast to convert the SIN into a biorefinery.

This paper illustrates the studies and partial results of the funded project BioMAN for the conversion of the old Mantova refinery into a lignocellulosic biorefinery, i.e., a second generation biorefinery (SGB). The revamping of the SIN will occur through the identification of the proper available biomasses, their possible transformation processes, the existing infrastructures and the bouquet of products of the local demand.

1.1 Biomass and Second Generation Biorefineries (SGBs)

Recent economic developments in many countries all around the globe have heightened the need for alternative energy resources due to the well-documented drawbacks of fossil fuels: (1) their finite supply (2) green house gases emission and global warming and (3) increasing price and unexpected fluctuations (Haghighi Mood et al., 2013). Such weaknesses have strengthened the interest in alternative, renewable, sustainable, and economically viable fuel. Conversion of renewable feedstock to liquid biofuels has become a promising method for the future (Fatih Demirbas, 2009).

Second generation biorefineries (SGBs) are particularly important in this scenario because of their economical, ecological and social role: they do not compete with other industry sectors for the use of sugar/starchy materials; instead, such industries use residual, low-valued and abundant products, such as non-food crops, agro-industrial residues (sugar-cane bagasse, cereal straw and leaves, corn cob) and forestry

residues (Fatih Demirbas, 2009). Such features allow for the valorization of such materials and their production chain as a whole.

2. Transformation Processes: Biorefinery Macro-Structure

A list of biorefinery products/processes is considered. Among its items are typical biorefinery products, such as bio-ethanol and green-diesel; there are products that can be incorporated by neighbor industries located at the Mantova SIN, such as bio-methanol and hydrogen; and there are other, less common, alternatives, such as xylitol or butene oligomers. Surely these products can be produced in an integrated fashion; therefore, the question to be answered is: what is the optimal operating point? What should be produced and how?

Figure 1 shows the different processes and their possible connections. Letters in italics represent products (intermediate and final); filled boxes represent final products; normal letters represent processes. A plus sign means different inputs may be offered for a process; a minus sign means the same input can be directed to different processes. Dashed arrows are used to avoid confusion in streams that cross over each other. In evidence is the production of bio-methanol, the results of which are reported further ahead in this work.

The scheme on Figure 1 is a prototype of a process integration model; since the outcome of a later stage may depend on actions taken at earlier stages, such a model is very complex. The difficulty in creating such a model is to be able to account for different operating conditions (temperature, pressure, catalysts, inputs and outputs) in each of the production steps.

A complete model will allow finding the operating optimum for the Mantova SIN or for any generic biorefinery. To do so it is sufficient to consider available infrastructure (vessels, towers, pumps, heat exchangers, etc.) when calculating CAPEX expenditures (i.e., costs of purchasing already existing infrastructure is zero). It is worth remembering that the use of already existing infrastructure restricts operating conditions (i.e. column size, number of trays, vessel volume, heat exchanger area, etc.) to the pre-existing ones.
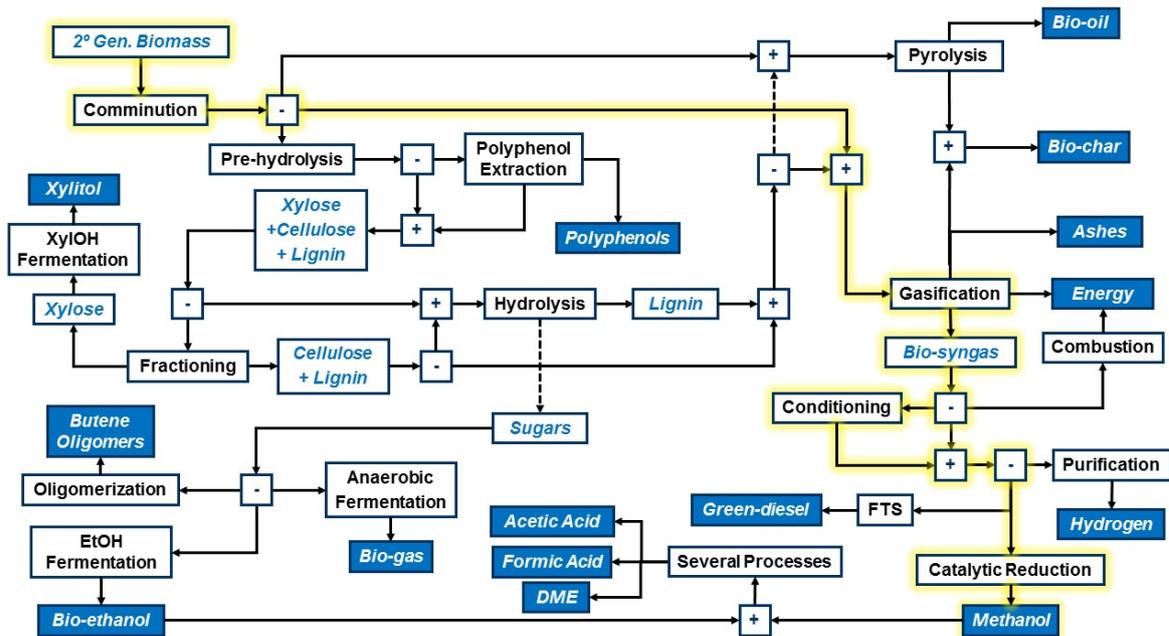

Figure 1: Biorefinery conceptual scheme. In evidence is the production of bio-methanol.

In the next sections the most important operations are described with more detail. Other operations, dubbed in Figure 1 as "Several Processes" (after methanol production) shall be researched with further depth in future works and are not mentioned here.

2.1 Pre-hydrolysis, Polyphenol Extraction and Fractioning

Pre-hydrolysis, also named 'pre-treatment' by some authors, is a process used to increase cellulose availability to enzymatic hydrolysis (Singh et al., 2015). Such operations disrupt the biomass matrix by acting on hemicellulose and/or lignin (Haghighi Mood et al., 2013), usually by hydrolysing the first of these components. Since the most abundant components of biomass are hemicellulose, cellulose and lignin, this operation basically generates a ('pre-')hydrolysate solution, usually composed by hemicellulose monomers (mainly xylose) and a solid fraction of lignin and cellulose.

According to Dario (2008), associated to the polymeric chains are small amounts of high added-value compounds called polyphenols. The same author showed that such compounds are released into the ('pre-') hydrolysate solution and they can be recovered with the aid of adsorption resins.

Fractionation is the name given in this work to the separation of the ('pre-')hydrolysate solution from the remnant solid fraction. This operation enables working with xylose and cellulose independently.

2.2 Hydrolysis, Butene Oligomerization and Fermentation

The term 'hydrolysis' usually implies cellulose hydrolysis, since hemicellulose is more easily degraded and with simpler processes than cellulose. This process can be realized by a number of means but is usually undertaken in acidic conditions or with the aid of enzymes. As reported above, if enzymes are used it is mandatory to have performed the pre-hydrolysis step. Badiei et al. (2014) report that if acid hydrolysis is performed pre-hydrolysis may be omitted, for both hemicellulose and cellulose can be hydrolysed simultaneously is conditions are severe enough. The same authors report that, among other problems with acid hydrolysis is the degradation of sugars which leads to the production of fermentation inhibitors such as furfural and hydroxymethylfurfural.

Such decomposition products are actually precursors to butene isomers in a process which passes first by levulinic acid and gammavalerolactone (Han et al., 2014). The same authors report that, in its turn, the butene isomers "can be oligomerized into larger molecular weight alkene species using a solid acid catalyst". These oligomers can be used as liquid fuel.

Different fermentation routes can be applied to biomass, the main restriction of which is that (hemi)cellulose be hydrolysed first. One of the main limitation of fermentation processes are purification costs. In xylitol production purification means evaporation/crystallization; for ethanol it means distillation; for bio-gas it means separating carbon dioxide from methane. Since lignin is not consumed in any of these fermentation processes (Malherbe and Cloete, 2002) it should be removed and destined either to gasification or pyrolysis.

2.3 Pyrolysis, Gasification and Combustion

Pyrolysis, gasification and combustion are all correlated transformations: the first occurs in the absence of oxygen, the last occurs with excess of oxygen; gasification is mid-way between both extremes. In each case, fluid-dynamics can be of one of several types: fixed bed, fluidized bed, etc; other parameters must also be considered (updraft, downdraft flow, etc.).

Pyrolysis can be used to produce solid, liquid or gaseous products. Since no oxygen is used, it requires a heating source, which can be provided by burning part of the products produced. Since gas-producing temperatures (as a main product) are around 1000 K (Calonaci et al., 2010), it is easier to produce gas by gasification, and gas-producing pyrolysis is not considered here. Therefore the only outputs considered in this operation are bio-char (solid) and bio-oil (liquid). Bio-char can be used as a fertilizer; bio-oil can be distilled to remove water and be used as a liquid fuel (Fatih Demirbas, 2009).

In SGBs, gasification is used to produce syngas, which is a mixture rich in hydrogen, carbon monoxide and carbon dioxide; a small amount of bio-char is also produced. If chemicals are to be produced, pure oxygen is preferred instead of air as the oxidant; as an inert, nitrogen is cumbersome in processes such as in fischer-tropsch synthesis (FTS) or methanol production, where gas compression is necessary. Lastly, since combustion of syngas presents several advantages over direct combustion (Di Blasi et al., 1999), only the first case was considered.

2.4 Conditioning, FTS and Catalytic Reduction

Conditioning operations are required for most operations with syngas, especially because it contains several impurities which may cause problems in downstream operations (Corella et al., 1998). Among such operations are tar abatement, water condensation and carbon dioxide removal. The water-gas shift reaction (WGSR), Eq(1), is also considered, for it adjusts hydrogen and carbon monoxide ratio:

$$H_2 + CO_2 \leftrightarrow H_2O + CO \tag{1}$$

Fischer-tropsch synthesis (FTS) is among the most developed strategies for producing liquid biofuels; its downside is the capital intensive nature of industrial plants that operate with this technology (Bond et al., 2014). This obviously reflects on final product price and ability to generate revenue.

Catalytic reduction of syngas to methanol is performed on a copper/zinc oxide catalyst supported on aluminium oxide (Manenti et al., 2013). Equations (2) and (3) show the possible conversion routes of syngas into methanol:

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

$$3H_2 + CO_2 \rightarrow CH_3OH + H_2O \tag{3}$$
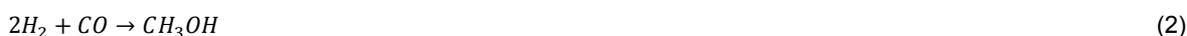
High pressures (above 50 bar) are used and gas compression, along with product purification (distillation) are important factors in quantifying revenues from methanol production.

3. Methanol Production

The study made on methanol production evaluated the techno-economic feasibility of producing 50 kt/y of methanol. The following steps were considered: gasification, gas conditioning, catalytic reduction and purification of final product. Among the gas conditioning operations there was tar abatement, water removal (condensation), the WGSR and two carbon dioxide removal steps (further dubbed 'amine stripping 1 and 2'). Costs involving each specific operation were computed with the aid of the procedures described in Turton et al. (2012).

3.1 Gasification

Arundo donax is a high productivity energy crop which is much diffused in all of europe and also in the Mantova region. Its average composition, obtained at Corno et al. (2014), was inserted into gasification simulator GASDS, which is described in detail by Ranzi et al. (2014). Simulation was performed with oxygen and steam as oxidizing components. To reach the objective of 50 kt/y of methanol the gasifier consumed approximately 159 kt/y of biomass, 53 kt/y of oxygen and 42 kt/y of steam. Gaseous input values were determined, by trial-and-error, after a few runs. The temperature of the gases at the entrance of was 800 K and exit temperature was 1600 K. Table 1 provides the composition of the gaseous stream exiting the gasifier.

Table 1: streams exiting the gasifier.

Component	CO	CO2	H2	H2O
Molar flow (kmol/h)	192,6	125,7	180,3	347,6

3.2 Gas Conditioning

Almost all of the gas conditioning operations were modelled in a commercial process simulator, with the exception of tar abatement, which was modelled as described by Pinto et al (2015): two catalytic beds, one with dolomite and another with a steam-reforming catalyst are considered after the gasifier. Since tar components amount to 1% in either mass or molar basis, no significant composition change was perceived after this operation.

The first amine stripping reduces CO_2 content on gas so that the WGSR equilibrium can be displaced towards hydrogen production. Another function of the amine stripping is removal of H_2S, which acts as catalyst poison in the WGSR. The remaining water is condensed and the second amine stripping further adjusts CO_2 concentration again. Table 2 summarizes the gaseous stream exiting each of the conditioning operations (all values are in kmol/h).

Table 2: streams exiting each of the conditioning operations (all values in kmol/h).

Process	CO	CO2	H2	H2O
Amine Stripping 1	192.6	12.6	180.3	347.6
WGSR	93.3	112.0	279.7	248.2
Water Removal	93.3	112.0	279.7	0
Amine Stripping 2	93.3	46.6	279.7	248.2

3.3 Catalytic Reduction and Purification of Methanol

The catalytic reduction of syngas and the purification of methanol was modelled with the aid of process simulator software PRO/II™. The gas stream exiting the second amine stripping (from gas conditioning) enters this process pressurized at 10 bar. After pressurization to 70 bar the syngas stream is fed to the catalytic reactor together with a recycle stream. After the methanol reactor two flash separators concentrate the product stream: the first separates the recycle and purge streams, the second separates excess carbon dioxide from liquid methanol and water. Lastly, water is separated from methanol by distillation. The process is illustrated on Figure 2: streams are reported in kylotons per year (kt/yr) while decimal numbers represent molar fractions.
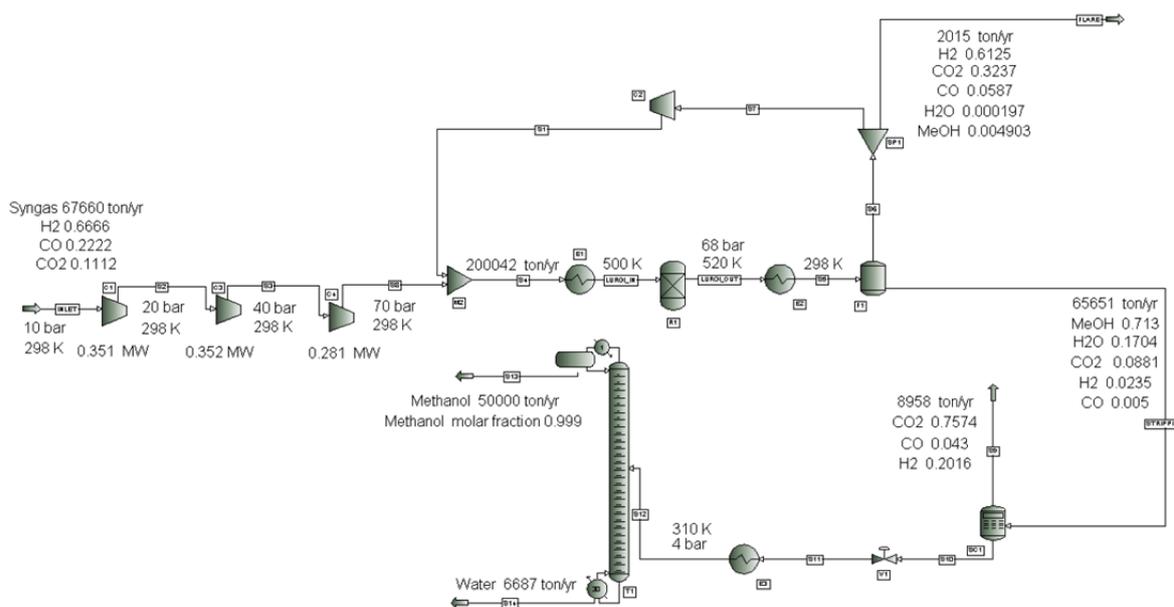
Figure 2: Catalytic reduction of syngas and purification of methanol using process simulator software PRO/II™.

3.4 Calculated Revenue

Total calculated revenue is the sum of expenditures/incomes in each individual step. As a simplification, no OPEX was considered (pumping and utility costs); catalyst costs on WGSR and tar abatement operations were computed by estimating a conservative monthly renewal of the catalyst charge; a conservative price of 20,000 €/t was estimated for these catalysts; the producing period considered was of 5 years. The calculated revenue on methanol production is summarized below on Table 3.

Table 3: methanol production revenues. Numbers inside parenthesis represent costs.

Component	Quantity (kt/y)	Yield	Unit Price (€/t)	Yearly Price (Mi €)	Total Price (Mi €)
Arundo donax	158.6	-	(45)	(7.3)	(36)
Oxygen	53.0	-	(160)	(8.3)	(41)
Steam	42.3	-	-	-	-
GASIFICATION					(0.4)
Bio-char	23.9	9%	600	14.0	70
Bio-syngas	230.0	91%	-	-	-
CONDITIONING					(10)
Syngas	67.7	29%	-	-	-
METHANOL PRODUCTION + PURIFICATION					(7.2)
Methanol	50.0	74%	400	20.0	100
CATALYSTS				(2.8)	(14)
TOTAL					61

4. Conclusions

A process framework was proposed for the establishment of an integrated biorefinery in the Mantova SIN based on stablished and emerging technologies. In future works, a further elaboration of such scheme will allow determining optimal operating conditions through optimization algorithms.

A preliminary economical assessment of methanol production was undertaken. OPEX costs were not considered but other conservative hypothesis were adopted: considered production time was of 5 years and catalyst/bio-char cost/selling price was relatively high/low. Despite such considerations, methanol production presented potential for revenue production: accumulated net income was 61 mi € with production of 50 kt of methanol per year. The yearly amount of biomass required is in agreement with current reports of local availability.

Acknowledgments

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