CHEMICAL ENGINEERING TRANSACTIONS

VOL. 37, 2014

Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus
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ISBN 978-88-95608-28-0; **ISSN** 2283-9216

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

DOI: 10.3303/CET1437051

Energy Efficiency Optimisation in Different Plant Solutions for Methanol Production from Biomass Gasification

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Methanol production from biomass gasification faces the problem of excess carbon, mostly carbon dioxide, in the produced synthesis gas. The stoichiometric ratio among hydrogen, carbon dioxide and carbon monoxide, required to optimise the energy efficiency of the process, can be achieved either by adding hydrogen produced by water electrolysis or by removing carbon dioxide through Rectisol process. These two processes are analysed and compared by means of a proper plant simulation. Moreover, methanol process demands a high amount of energy to get an almost pure product, implying elevated investments. Pinch analysis has been applied to minimize this energy consumption, designing an optimised heat exchanger network and investigating thermal integration opportunities among different sub-processes.

1. Introduction

Nowadays fossil fuels such as oil, natural gas and coal are the main source of energy in the world. Their use has increased the amount of carbon dioxide in the atmosphere contributing to global warming. Biomass is considered to be one of the most important renewable energy sources for this century (Boerrigter and Rauch, 2006), to replace fossil fuels without increasing greenhouse gas emissions. It is used for energy generation, the production of chemicals products and biofuels. An increase of these fuels production and use is expected with the introduction of second generation biofuels from gasification of lignocellulosic biomass, such as dimethyl ether, methanol, hydrogen, Fischer-Tropsch diesel or synthetic natural gas (Heyne, 2010). Among these candidates, methanol has the potential to have a promising future. Since this compound is liquid at room temperature and pressure, it can be easily stored. It may be used as fuel in adaptable combustion engine today, or in fuel cell powered cars in the future (Specht et al., 1999).

The aim of this paper is to design an useful model of methanol production from gasification of lignocellulosic biomass, considering different plant solutions in order to optimise the energy efficiency of the process.

2. System simulation

Aspen Plus has been selected to model methanol production from biomass gasification. It is a comprehensive chemical process modelling system, used to design and improve process plants. Figure 1 presents the flow sheet of the process. The grey area represents the stoichiometric adjustment unit discussed in § 2.2 and its configuration depends on the plant solution adopted (Rectisol process or hydrogen addition).

The model starts with a gasifier fed with pure oxygen and steam, used as oxidizing agents, and biomass. The feed is 1000 t/day biomass, order of magnitude of Awirs thermal plant, running near Liege and managed by Electrabel company. Biomass moisture is 10% wt on a dry basis, because a moisture content of 10-20% wt is advantageous to produce a product gas with a high heating value (Gustafsson, 2011). For mass and energy balancing purpose, dry biomass can be assimilated to cellulose and represented by smaller molecules with a similar overall composition $C_xH_yO_z$. In particular, two possible feedings have been considered: Biomass 1 will be modelled as acetic acid ($C_2H_4O_2$) and Biomass 2 as acetic anhydride ($C_4H_6O_3$). Additional components are added to the feed to generate secondary products such as sulphur, chlorine and nitrogen.

Please cite this article as: Puerari F., Bosio B., Heyen G., 2014, Energy efficiency optimisation in different plant solutions for methanol production from biomass gasification, Chemical Engineering Transactions, 37, 301-306 DOI: 10.3303/CET1437051

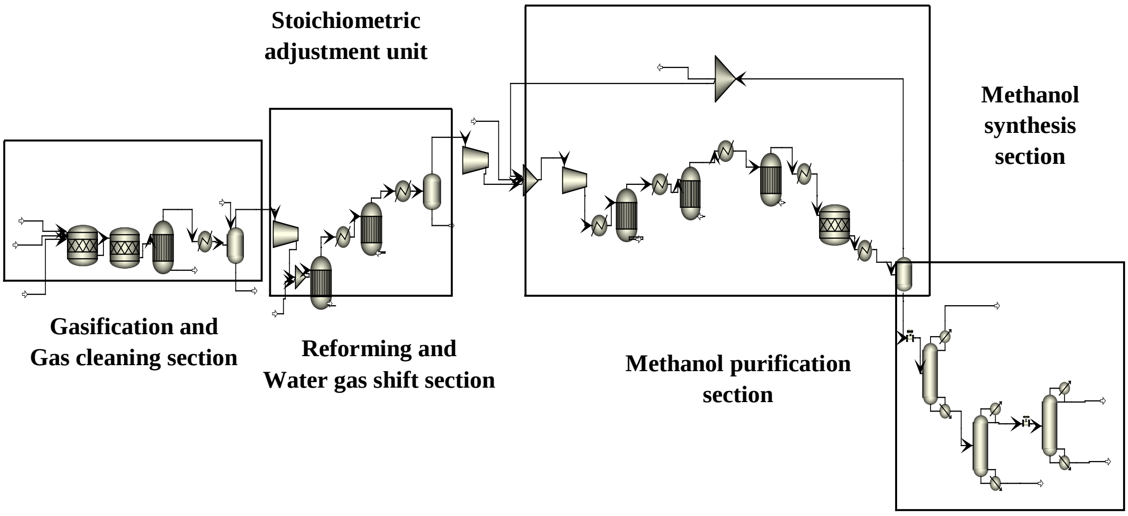

Figure 1: Methanol process flowsheet using Aspen Plus software.

Different amount of steam have been investigated and the best results have been obtained with a flow rate of 4166.67 kg/h: with higher value more unwanted CO_2 is produced instead of CO and hydrogen and with lower value the gasifier can rust due to carbon deposition. This amount of steam is generated inside the process.

The oxygen is produced by water electrolysis with a flow rate of 1074 kmol/h, considering an electrolyser efficiency of 68% (Zoulias et al., 2002). This amount is enough for the process. A hydrogen flow rate of 2149 kmol/h is produced as well.

2.1 Biomass gasification

The process of biomass gasification may be represented by the reactions given in Table 1. In Aspen Plus, the gasifier can be modelled as a sequence of three adiabatic reactors operating under 10 bar. The first two reactors are standard modules called RSTOIC, that are stoichiometric reactors based on known fractional conversion. The first RSTOIC models combustion reactions, biomass degradation and production of by-products (R1, R2, R3, R4 and R5 in Table 1). Most of biomass is converted into syngas, but some secondary reactions must be taken into account: part of biomass "distils", cracking reactions produce tars (modelled as naphthalene and methyl phenol); part of the carbon contained in the biomass forms char (modelled as C). The second RSTOIC reactor is inserted in order to convert the remaining biomass into methane and carbon dioxide (R6). In the third reactor (type REQUIL, equilibrium reactor), methane steam reforming and water gas shift reactions are brought to equilibrium assuming adiabatic conditions (R7 and R8). The presented approach fits the aim to preliminarily assess advantages and disadvantages of the selected technologies for methanol production, while the integration in the model of more detailed kinetic schemes could be of great interest for a deeper study of the gasification step (Ranzi et al., 2014).

Oxygen flow rate is adjusted to reach 850°C at the outlet of the third reactor, adding a Design Specification to the Aspen model. After gasification step, the products are cooled down to 400 °C in a heat exchanger; heat recovered at 30 bar allows to obtain saturated steam. Char, tar and other impurities are removed in a washing column using heavy oil ($C_{30}H_{62}$) as solvent. The quench outlet temperature is 80 °C.

Table 1: Gasification reactions

Reactions	Reaction number
Biomass + $O_2 \rightarrow CO_2 + H_2O$	R1
Biomass $\rightarrow C_{10}H_8 + CO + CO_2 + H_2O$	R2
Biomass $\rightarrow C_7H_8O + CO + H_2O$	R3
Biomass $\rightarrow C_2H_6 + CO + CO_2 + H_2O$	R4
Biomass $\rightarrow C + CO_2 + H_2O$	R5
Biomass $\rightarrow CH_4 + CO_2$	R6
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	R7
$CO + H_2O \leftrightarrow CO_2 + H_2$	R8

2.2 Steam reforming and water gas shift sections

After the washing column, the clean gas is compressed to 30 bar before entering the reformer. Methane and ethane, representing a significant part of the heating value of the gas, are reduced by reforming with steam at 900°C and 30 bar to produce additional syngas. Other steam is added with a flow rate of 3000 kmol/h to reach a ratio H_2O/C about 3.5, avoiding coke formation and moving the equilibrium towards the products. The reactions, shown in Table 2, take place in the reactor. The steam reforming reaction is favored at low pressures, but elevated pressures allow to get economic benefits (smaller equipment). Methanol synthesis also takes place at high pressures (Manenti et al., 2013). Afterwards the synthesis gas is cooled down to 220 °C and is fed to water gas shift unit. Since the gasification of woody biomass produces a gas mixture of CO, CO_2 and H_2 deficient in hydrogen, water gas shift reactor is used to increase the hydrogen production and the ratio H_2/CO, which has to be greater than 2 (Specht et al., 1999). The reaction (R8) proceeds to completion at low temperatures and is independent of pressure.

Table 2: Steam reforming and water gas shift reactions

Reactions	Reaction number
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	R7
$CO + H_2O \leftrightarrow CO_2 + H_2$	R8
$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2$	R9

2.2 Stoichiometric adjustment unit

Before methanol synthesis, a favourable stoichiometric ratio (FSR) of H_2, CO and CO_2 is required in order to get the highest yield of methanol (Lee et al., 2007). Eq.(1) shows the ideal value of this ratio.

$$FSR = \frac{x_{H_2} - x_{CO_2}}{x_{CO} + x_{CO_2}} = 2 \tag{1}$$

Where x is the molar fraction of the components in the mixture. If the stoichiometric does not reach the value desired for the process after water gas shift reactor, a stoichiometric adjustment unit is inserted in order to optimise the energy efficiency of the process. Table 3 shows this stoichiometric ratio after water gas shift reactor, using different biomass models.

Table 3: Stoichiometric ratio H_2, CO and CO_2 after water gas shift reactor

Parameter	Biomass 1	Biomass 2
Stoichiometric ratio H_2, CO and CO_2	0.25	0.38

As shown in Table 3, the ratio does not reach the value required, hence hydrogen addition and Rectisol process have been investigated as different plant solutions.

Rectisol process is a carbon dioxide removal process based on physical absorption of the gas in methanol solvent at low temperatures. It is designed into two sections: two absorption columns and two separators for the solvent regeneration (Figure 2). The crude syngas feed is cooled to -21°C for Biomass 1 and -23°C for Biomass 2 and sent into two absorption columns. A different inlet temperature is used for the second model, due to the higher content of CO_2 respect to the first one, in order to capture more CO_2. The methanol solvent temperature and pressure are -60°C and 30 bar respectively (Preston, 1982). The solvent is split into two parts: a mole fraction of 0.1 is fed to the first absorber and the second part is fed to the other column (Preston, 1982). The purified syngas is retrieved from the top of the second absorber. The rich solvent streams, exiting from the absorption columns, are mixed and sent to the solvent regeneration system. Two separators are added to release the captured CO_2 from methanol and for solvent regeneration. The units work at different pressure: in the first one the most part of CO_2 is separated from methanol at 10 bar; in the second one the last part of light gases is released at atmospheric pressure to recycle an almost pure solvent. These pressures allow to obtain an efficiency of solvent recovery above 97%. The stoichiometric ratio H_2, CO and CO_2 after Rectisol process is about 1.78 for both biomass models.

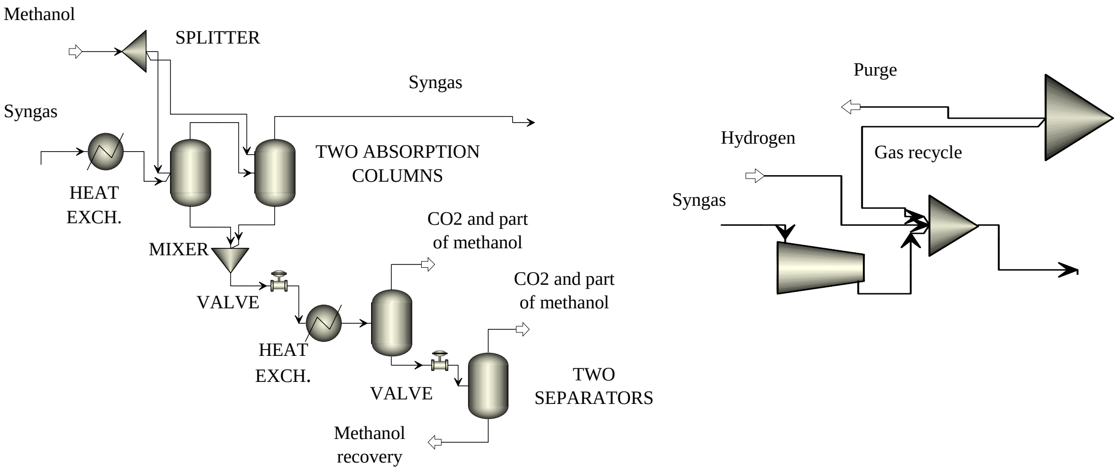

Figure 2: Flow sheet of the adopted plant solutions: Rectisol process (to the left) and hydrogen addition (to the right).

The other plant solution is hydrogen addition, produced by water electrolysis, to compensate the excess carbon dioxide for CO_2 hydrogenation. Adding a flow rate of 2100 kmol/h, the stoichiometric ratio H_2, CO and CO_2 is about 2 for both biomass models. This flow rate cannot be overcome due to the maximum hydrogen flow rate produced by water electrolysis, using the assumptions previously described. It is mixed with the syngas and the unreacted gas recycle of the process before methanol reactors, in according to the highest methanol production (Figure 2).

2.3 Methanol production and process energy efficiency

The methanol synthesis reactors are modelled as a sequence of four adiabatic reactors. The first three reactors are REQUIL type and model the methanol synthesis reactions (R10 and R11 in Table 4). The syngas feed is compressed to 70 bar (process becomes too expensive with higher pressure) and heated to 200°C in according to the best methanol production. After each reactor, a heat exchanger is inserted to bring the temperature down to 200°C. The temperature changes because of the exotermic reactions that take place inside the reactors. The last reactor is RSTOIC and models the major side reactions of methanol synthesis: DME synthesis (R13) and ethanol synthesis (R12). The reactions are given in Table 4. The conversion into methanol is very low, for this reason it is necessary to insert a recycle (Kansha et al., 2013). After the four reactors, a separator is added in order to separate the light gases (inert gases and unreacted compounds) from the product, which is cooled to 30°C. Part of the recycle is purged to remove inert gases like methane, which affects negative to the fuel production efficiency.The crude methanol from the synthesis loop contains water and by-products. The purification is achieved using three distillation columns in series. In Aspen Plus, the distillation columns have been modelled as RadFrac blocks (rigorous 2 or 3 phase fractionation for single columns). A valve is inserted to decrease the pressure to 10 bar, the working pressure of the distillation columns. After the separator, the heat exchangers are not needed because the temperature is in the range of distillation temperatures. The first column is used to remove light gases (mainly composed by CO_2 and DME) from methanol, ethanol and water. In the second column methanol and ethanol, more volatile than water, exit at the top and the water at the bottom reaching a purification about 99.5%. To obtain higher purification, a final distillation column can be inserted to separate ethanol and the remaining water from methanol. After three distillation columns, the methanol purity overcomes 99.98%.

Table 4: Reactions taking place in methanol reactors

Reactions	Reaction number
$CO + 2H_2 \leftrightarrow CH_3OH$	R10
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	R11
$CO + 2H_2 \leftrightarrow C_2H_5OH + H_2O$	R12
$2CH_3OH \leftrightarrow (CH_3)_2O + H_2O$	R13

After methanol purification, the last step is the calculation of the process energy efficiency. It relates the thermal power of all useful products (methanol, DME and ethanol) to the power input (feed and external fuel). The feed and external fuel are considered in terms of biomass and hydrogen respectively. In the process with hydrogen addition, the energy efficiency is reduced due to the relatively inefficient electrolyser. It is assumed an efficiency of 68 % for the alkaline water electrolysis unit (Zoulias et al., 2002).
The data obtained, at the end of the process, are shown in Table 5. Diverse results have been found, using different plant solutions and biomass models.

Table 5: Methanol production and purity and energy efficiency at the end of the process, using different plant solutions (between parenthesis) and biomass models

Parameter	Biomass 1 (CO_2 removal)	Biomass 1 (H_2 addition)	Biomass 2 (CO_2 removal)	Biomass 2 (H_2 addition)
Methanol production (kmol/h)	422.7	1025.8	509.3	1209.5
Methanol purity	0.9999	0.9998	0.9999	0.9999
Process energy efficiency	54.86 %	67.85 %	55.59 %	72.73 %
Process energy efficiency (with electrolyser)	54.86 %	55.13 %	55.59 %	60.23 %

3. Pinch analysis

Pinch analysis is a methodology used to minimize the energy consumption of industrial plants. It determines the minimum heating and cooling demand and number of heat exchangers for industrial processes without having to specify any heat exchanger network (Douglas, 1988).The Grand composite curve is defined, using Hint software, from the process data in according to a fixed minimum temperature difference (ΔTmin) between the hot and cold streams in the heat exchanger. ΔTmin is chosen to determine the optimal size of the exchanger. In this analysis the ΔTmin is 10 K, a value commonly used in the chemical processes (CANMET, 2003). The Grand composite curve shows the minimum energy requirements for the process and the pinch point. This point divides the process into two independent parts: a heat source below the pinch temperature and a heat sink above. Between these two parts, there is no heat exchange. With the chosen ΔTmin value the pinch temperature is 1168 K: 1173 K for the cold streams and 1163 K for the hot ones (Figure 3). To avoid energy penalty, distillation columns do not fall across the pinch point but below it (Douglas,1988). The minimum heating and cooling demand is calculated by Hint program (Table 6).

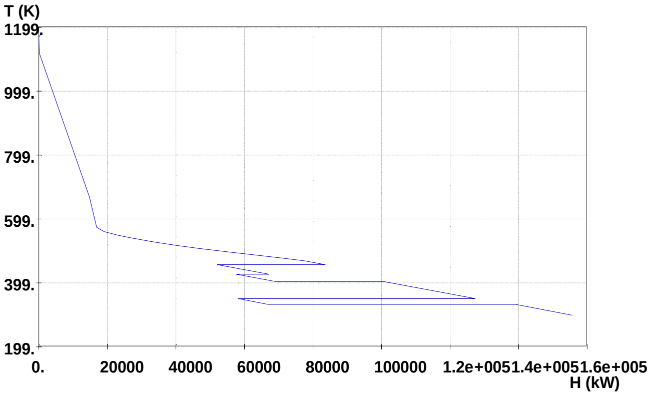

Figure 3: Grand composite curve for the methanol process with Biomass 1 and hydrogen addition (from Hint program).

Table 6: Minimum heating and cooling demand in methanol process, using different plant solutions (between parenthesis) and biomass models

Demand	Biomass 1 (CO_2 removal)	Biomass 1 (H_2 addition)	Biomass 2 (CO_2 removal)	Biomass 2 (H_2 addition)
Heating (kW)	627	627	668.269	668.269
Cooling (kW)	85409.3	145945	92778.2	161974

The following step of the analysis is to design a heat exchanger network (HEN), which reaches the energy targets with the minimum number of heat exchangers. The calculation suggests: nineteen heat exchangers for the process with carbon dioxide removal and seventeen heat exchangers for the process with hydrogen addition. Finally, in methanol process most of the streams are hot streams, hence it is possible to recover heat and produce steam inside the process. The steam cycle is represented by a separate curve (utility) integrated to the Grand composite curve. Steam production at different saturated pressures has been investigated, in order to optimize the steam power cycle to produce heat and power from the excess heat of the process. The best steam production is 20.3 kg/s, obtained in the process with Biomass 2 and hydrogen addition at 20 bar and 485.57 K. This amount is able to feed the gasifier and the reformer, which require a total steam flow rate of about 15 kg/s. The remaining part can be used to produce additional energy, increasing the energy efficiency of the process.

4. Conclusions

The results of this work show that the choice of the starting biomass is important, because Biomass 2 allows to obtain a production of about 19% more than Biomass 1, due to its higher energy content. Considering the different plant solutions, a higher production of methanol has been obtained using hydrogen, because it meets the required stoichiometric ratio for the process and allows a nearly complete utilization of the carbon contained in the biomass. In particular, an energy efficiency of about 73% has been achieved for the methanol process with Biomass 2 and hydrogen addition; it represents the highest value obtained. However, the total energy efficiency has been reduced from 73% to 60% due to the relatively inefficient electrolyser. To avoid a decrease of the efficiency, the energy needed for the electrolysis unit may be retrieved from an additional production of energy by using the steam produced inside the process. After Aspen Plus simulation, the pinch analysis has been carried out with Hint software to minimize the energy consumption of the process. The heat exchanger network has been designed reaching the energy targets with the minimum number of heat exchangers suggested by the program. In methanol process a lot of heat is released, hence steam production at different saturated pressures has been investigated in order to optimize the steam power cycle to produce heat and power from the excess heat of the process.

In conclusion, the process of methanol production from biomass gasification has been proven convenient and Interesting elements have been provided to support the choice of the process.

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