CHEMICAL ENGINEERING TRANSACTIONS
VOL. 39, 2014

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

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong
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ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI:10.3303/CET1439204

Solar-Supplied Biomass Gasification for the One-Step Synthesis of Methanol and Dimethyl Ether

Flavio Manenti*, Andres R. Leon-Garzon, Francesco Rossi, Zohreh Ravaghi-Ardebili, Sauro Pierucci

Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
flavio.manenti@polimi.it

The integration of novel processes and technologies in a sustainable way with the purpose of achieving a greater energy-process intensification will be beneficial in chemical and process engineering from both the economic and environmental point of view. Especially, it would be really advantageous to employ a combination of various energy sources (renewable and non-renewable) or minimum CO_2 emission pathways in the chemical process industry. Owing to this, power generation from clean and emission free sources plays a key role in the sustainability of an intensified process. Particularly, there is a need to provide energy in form of steam from alternative sources rather than from traditional or common technologies. A concentrated solar power (CSP) plant is proposed in the present paper as a potential process for power generation. Afterwards, a biomass gasification process driven by solar energy to produce syngas is suggested. The resulting syngas can be employed as a chemical, fuel or energy vector. However, one obstacle is to deal with the operating temperature of the gasification process that commonly varies from 750 °C to 1,000 °C, while the steam generated in a solar plant is slightly over 400 °C. Therefore, the various effective parameters and operating conditions in the gasification process should be taken into account to address the drawbacks encountered in a low temperature operation in order to accomplish the goals of the process. Finally, this solar driven gasification process is coupled with a methanol/dimethyl ether production unit establishing a renewable pathway for chemical production independent of fossil fuel back-up through the process.

1. Introduction

Replacing the existing power generation system relying on traditional energy sources with renewable power generation systems can bring several economic and environmental benefits. Environmentally speaking, reducing the carbon footprint from existing chemical plants does not only require an extensive reduction of the energy requirements within the same but also reducing the carbon emissions associated with auxiliary units. Due to the fluctuations in oil price; the introduction of more stringent environmental protocols; and the growing interest in renewable energy sources, it is worth to focus on power generation systems independent from fossil fuel resources. Operationally speaking, steam is usually obtained from boilers running on coal-fired or natural gas-fired burners. Modifying the process to alter the relative energetic requirements is an approach for energy reducing purposes (Xu and Wiesner, 2012). As a result, steam generated from solar energy is a promising alternative to the traditional power generation systems. One advantage of solar generated power is its storage capability, whether other renewable energy sources (e.g. wind-power) fall short on this. Therefore, a reliable storage technology for this complex and dynamic process must be designed, modelled and simulated (Powell and Edgar, 2012). Figure 1 shows a typical two-tank direct storage for a concentrating solar power (CSP) plant (more details on the process can be found in Vitte et. al. (2012); and on the process modelling in Manenti and Ravaghi-Ardebili (2013)). The energy storage must guarantee a continuous power provision, but operating completely independent on co-fuel support throughout the day and night. Figure 2 illustrates the temperature profile of the steam generated by the CSP plant. The produced steam can be employed afterward either to generate power or to supply downstream units like the biomass gasifier considered in the present work.

Please cite this article as: Manenti F., Leon-Garzon A.R., Rossi F., Ravaghi-Ardebili Z., Pierucci S., 2014, Solar-supplied biomass gasification for the one-step synthesis of methanol and dimethyl ether, Chemical Engineering Transactions, 39, 1219-1224 DOI:10.3303/CET1439204

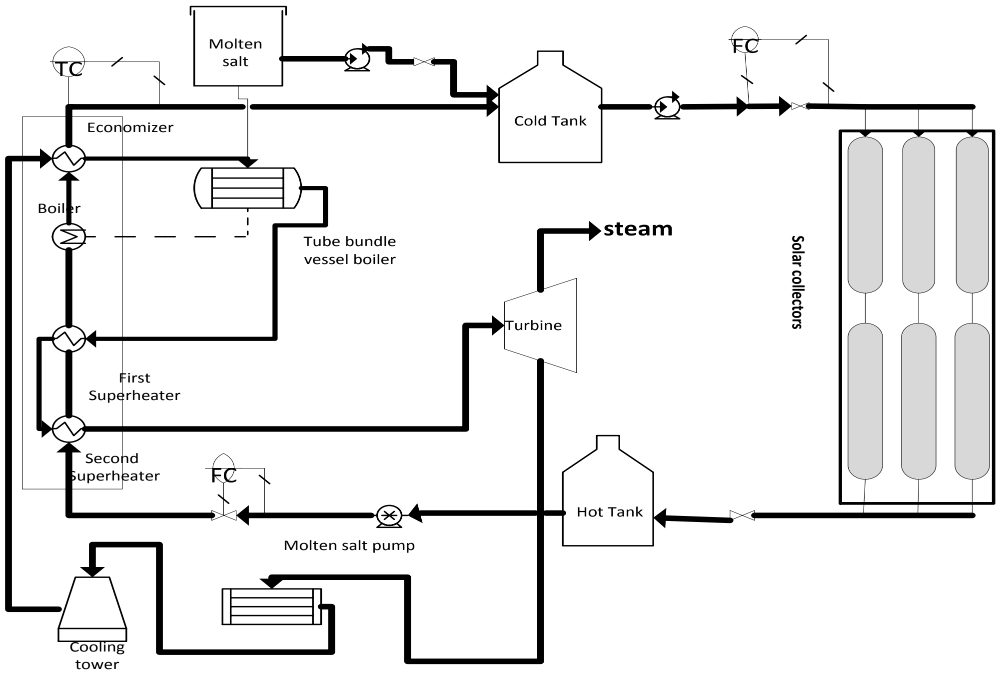

Figure 1: Flowsheet of the concentrated solar power (CSP) plant for power generation

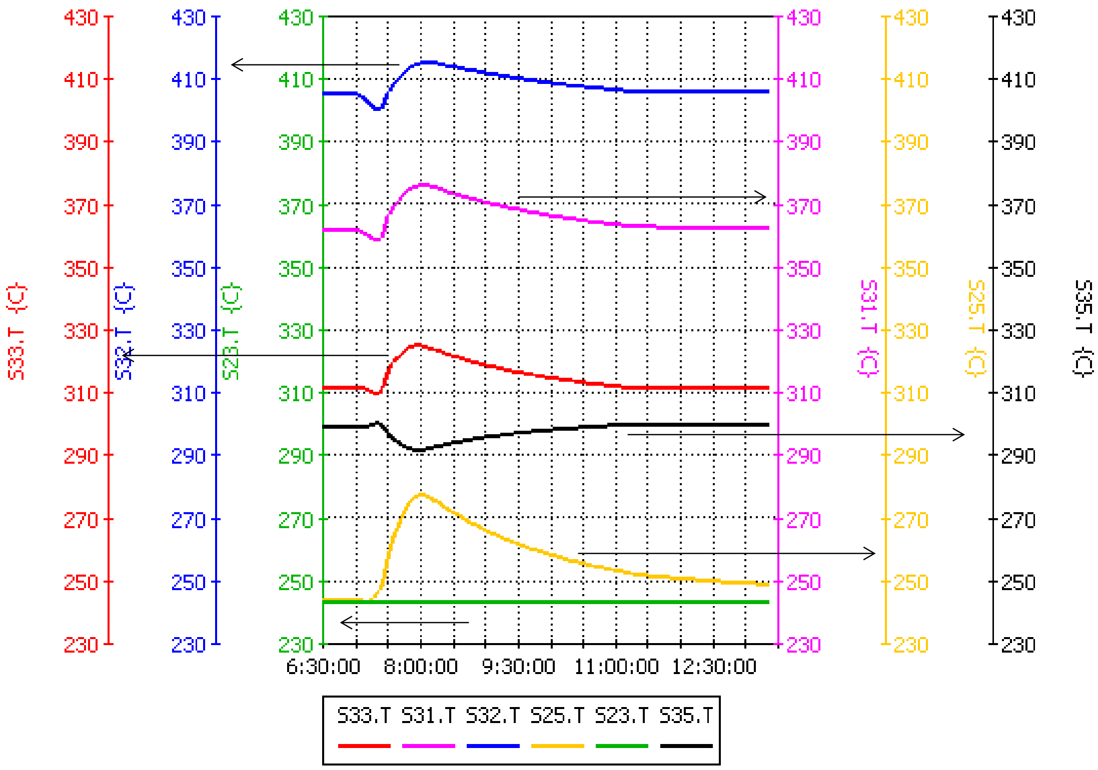

Figure 2: Temperature profile of: (S23.T) fresh water supplied to the heat exchange network; (S35.T) water outflowing the economizer; (S33.T) steam outflowing the boiler; (S31.T) steam outflowing the first superheater; (S32.T) steam outflowing the second superheater; and (S25.T) expanded steam leaving the turbine and sent back to the economizer

2. Biomass Gasification

Although there are still abundant coal reserves geographically widespread all over the world, due to its higher, price in comparison with oil and natural gas, and the environmental issues related to its consumption, coal is not well positioned as an emission free and inexpensive feedstock in front of the so-called renewable energy sources (Demirbas, 2004). In fact, taking advantage of the flexibility of the gasification process (Fan et al., 2008) there is a motivation in employing renewable energy sources such as biomass in such process with a sustainability level similar or even superior to the equivalent coal-based gasification. Biomass is a promising renewable resource and current research activities are focused towards the production of bio-products and biomass derived fuels. On the other hand, gasification is the process of converting solid feedstock into useful gaseous fuels or chemicals through partial oxidation (Badeau and Levi, 2009). Such products can be employed either as energy vectors or used in the synthesis of value-added chemicals (Basu, 2010). Generally speaking, gasification is defined as the endothermic chemical process occurring at temperatures greater than 650 °C that breaks down organic materials into gaseous species such as H_2O, CO_2, CO and CH_4 and solid char. Therefore, the main drawback of supporting the gasification process via a concentrated solar power plant (Figure 3) would be the low temperature reached by the steam.
In order to adopt the solar driven gasifier, it is necessary to adjust the operational conditions; select the appropriate configuration of the gasifier, pre-treatment of feedstock; and more importantly re-design the reactor for this novelty (Ravaghi-Ardebili et al., 2014). As already explained, gasification is an overall endothermic process that employs oxygen for the partial oxidation (an exothermic reaction) of the feedstock; and water for the gasification (an endothermic reaction) of the same, thus it is possible to exploit the oxygen intake to sustain the low temperature process with the combustion of the biomass. On the other hand, the nature of the feedstock affects the yield of the produced syngas and the efficiency of the process as well. Thus, as the synthesis gas produced is going to be used downstream to produce value-added chemicals, increasing the yield of CO and H_2 while keeping special attention to the H_2:CO is desirable. Therefore, a design policy must be chosen (see Table 1) to approach a desired H_2:CO ratio when employing biomass as feedstock, by adopting a rigorous mathematical model of the gasifier (Sommariva et al., 2011), and analysing the effect of operating parameters (Corbetta et al., 2014).

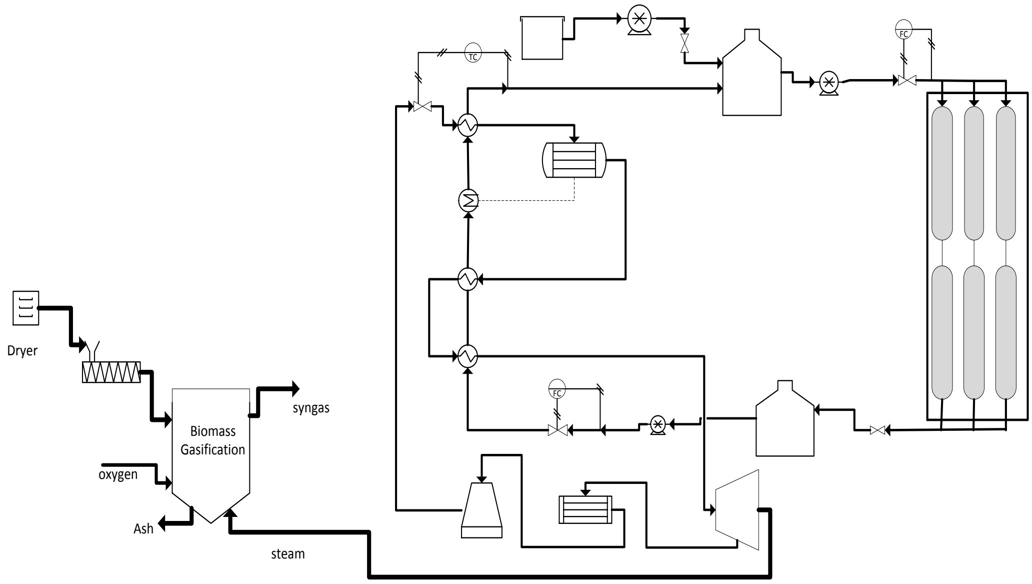

Figure 3: Flowsheet of the integrated biomass gasification with a concentrated solar power (CSP) plant

Table 1: Operating condition of the adopted gasification unit

Biomass	
Ultimate Analysis	
C	51 %
H	6.1 %
O	42.9 %
HHV	20.43 MJ/kg
POWER	267.6 MW
Particle Specifications	
Density	1,250 [kg/m^3]
Porosity	30%
Humidity	7%
Diameter	8 mm
Reactor	
Surface	3 m^2
Height	4.m
Flow rate of biomass	47,000 kg/h

3. Methanol/Dimethyl ether Synthesis

Methanol is one of the most common and basic hydrocarbon chemicals produced nowadays. Demand in methanol production increases an average of 10 % per year since 2010; hence contributing to the high expectation of a sustained growth for this decade. Approximately 27 % of the world's production of methanol is employed as a raw material for formaldehyde synthesis followed by its direct use as a fuel with 11 %; finally the third largest consumer of methanol is the acetic acid production industry. Methanol can be obtained from several sources and routes, starting from fossil-fuels via syngas conversion, passing by the selective oxidation of methane (from natural gas) to the reductive conversion of atmospheric carbon dioxide with hydrogen (Olah et al., 2006). Nevertheless, methanol synthesis is almost exclusively produced via syngas from fossil fuel resources, a well-known process characterized by its low yield (about 7 % molar of methanol production per reactor pass due to thermodynamic equilibrium limitations according to Manenti et al., (2013)). Even so, it is still possible to couple methanol synthesis with the simultaneous production of other interesting products in order to shift the equilibrium thermodynamics. One possibility is to employ a bifunctional catalyst to simultaneously produce methanol and dimethyl ether (DME); this latter considered a promising diesel fuel substitute. Such technology is usually called direct dimethyl ether synthesis (Manenti et al., 2014). One advantage of DME is its low NOx combustion emission, with no particulate matter or SOx production in comparison with traditional diesel fuel (Clausen et al., 2011). It is then possible to produce methanol and DME from biomass via gasification and several routes are possible, involving either conventional, commercial, or advanced technologies, which are currently under development. Facilities for syngas production via gasification typically consist of the following basic steps: feedstock pre-treatment, feedstock gasification, gas cleaning, gas reforming to adjust the H_2:CO ratio, and gas separation or purification. Syngas produced from biomass is not suitable for methanol production (ideally H_2/CO~2) as it is significantly lower in comparison with syngas obtained from other sources (e.g. coal or natural gas) (Li et al., 2010). Therefore, the procedure to adjust the value of the H_2:CO ratio to a more favourable value is particularly important. For this purpose, syngas from biomass is conducted into a water gas shift and steam-reforming reactor to promote the production of hydrogen and carbon monoxide. It is then possible to produce methanol and DME conducting the adjusted syngas is into the shell side of a gas cooled reactor, where is pre-heated by a hot stream flowing within the tubes as seen in Figure 4. The pre-heated syngas is then fed to the tube side of a water cooled reactor, filled with bifunctional catalyst. The syngas is partially converted into methanol and DME along the first reactor. The methanol/DME synthesis is particularly exothermic and the shell side is filled with boiling water to preserve the desired operating conditions of the water cooled reactor. The intrinsic intensified nature of modern methanol synthesis allows combing the reactor system to medium pressure steam generation. The stream leaving the water cooled reactor is fed to the tube side of the gas cooled reactor where the methanol/DME synthesis continues. The temperature inside the tube side of the gas-cooled reactor is controlled by exchanging with the fresh inlet syngas to be pre-heated flowing in counter current in the shell-side.

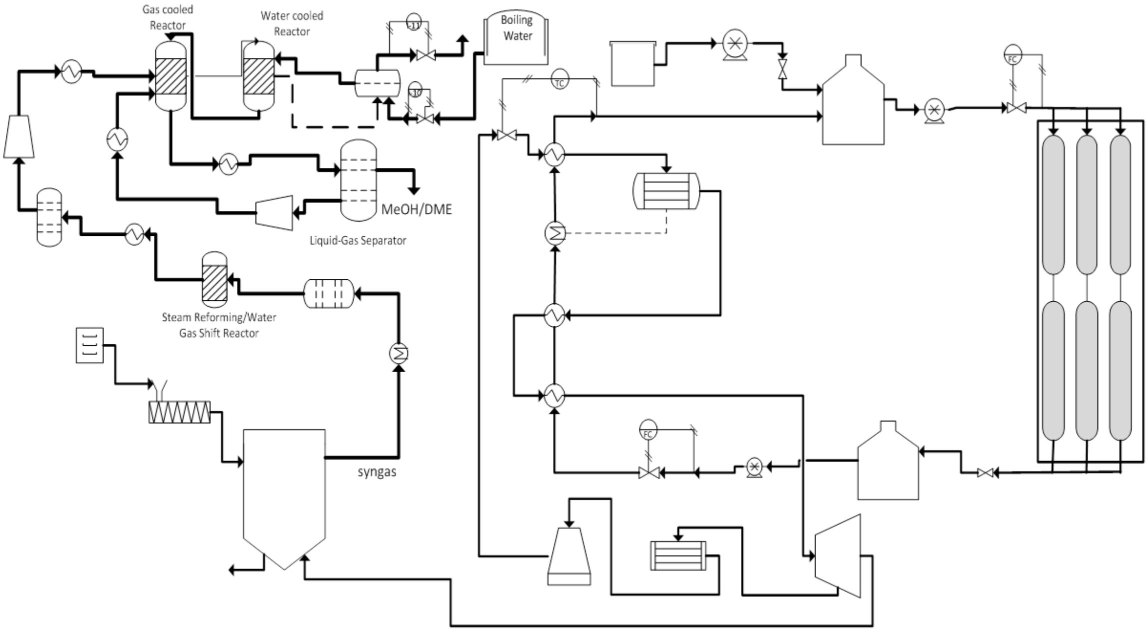

Figure 4: Flowsheet of biomass-to-methanol/DME process (the renewable pathway)

The stream leaving the gas cooled reactor is then sent to a downstream separation unit to recover the methanol/DME and the unreacted syngas, which is recycled back to the reactor except for a purge to avoid the accumulation of incondensable gases (Manenti et al., 2014).
The methanol and dimethyl ether mole fraction profile along the reactor is reported in Figure 5. The methanol yield is typically affected by thermodynamic equilibrium limitations, nonetheless coupling the dimethyl ether synthesis into the system results in a synergistic interaction capable of alleviating in some extent the detrimental effects of equilibrium thermodynamics of the methanol synthesis reaction; It is worth noting that due to the strong exothermic nature of the reaction a proper temperature control must be exerted to avoid catalyst deactivation by sintering.

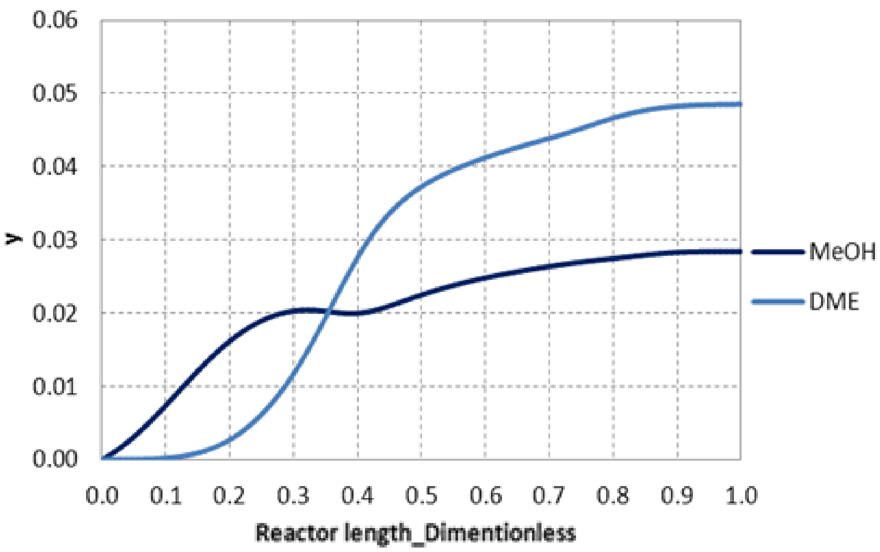

Figure 5: Methanol/DME production from the designated and proposed plant

4. Conclusions

The overall methanol/DME synthesis process is modelled, simulated and integrated with a concentrated solar power (CSP) plant aimed to generate low temperature steam. The generated steam in the CSP is employed to support a low-temperature biomass gasification process in order to produce syngas. However, according to the syngas application, which in this work is aimed towards the synthesis of methanol and DME, the H_2:CO ratio must be adjusted in a water gas shift/steam reforming reactor. Thus, the resulting integrated process is a green, sustainable and innovative way for the production of valued-added chemicals such as methanol/DME. The conception of the process is a result of the involvement of several abilities and knowledge in process engineering in order to design, adjust and combine different units; and especially employing green and renewable sources of energy through the whole process. The main issues encountered throughout the activity of modelling and studying the practical feasibility of this novel solar-driven route from biomass to methanol/DME were related to the need of different tools and interdisciplinary competences to accomplish it.

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