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Analysis of methanol production from bio-syngas through an innovative reactor

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This work aims to develop a novel co-generative technology to produce methanol through bio-syngas from waste biomass. To this aim, residual biomasses in southern Italy will be characterized by proximate and ultimate analyses and used as fed in syngas production for methanol synthesis. A non-stoichiometric method based on Gibbs free energy minimization was used to simulate biomass steam gasification and subsequent syngas adjustment through WGS reaction. The processed syngas are fed to a methanol reactor consisting of a membrane for water separation, an electrolyzer splitting the water produced by methanol synthesis, and a heat exchanger for heat recovery integrated into one equipment. By this reactor, methanol production yield is studied for several gasified biomasses.

* 1. Introduction

Methanol is a promising energy vector with a worldwide increasing demand, and, as a raw material, it is used as a feedstock to synthesize many chemicals such as formaldehyde, acetic acid dimethyl and methyl tertiary butyl ether. Additionally, due to its high-octane content, methanol plays a crucial role as a synfuel, e.g., in biodiesel production and direct gasoline blending (Sarvestani et al., 2024). Commercially, methanol is produced from syngas through three main stages: syngas production through natural gas reforming, methanol synthesis, and purification. Syngas production is unquestionably the most expensive step in this production chain since it is an energy-intensive process; conventional methanol production emits between 20.9 and 45.4 kg CO2/GJ depending on the process configuration and feedstock (Kafrudi et al., 2022). So, it is necessary to identify new processing routes and raw materials to reduce greenhouse gas (GHG) emissions and meet the IPCC and COP27 goals (Moosman et al. 2022). In this context, starting from renewable sources, methanol production could be a new route to achieve these objectives. Natural gas can be substituted by biomass that produces bio-syngas containing hydrogen, carbon monoxide, carbon dioxide, and methane through gasification. As a sustainable and climate change-neutral fuel, biomass is increasingly considered a competitive energy source. Biomass can be converted into added-value products similar to fossil fuels and power. The biomass-to-methanol process may be essential in introducing renewables in the industry chain for chemical and fuel production (Gautam et al. 2020). CO and CO2, primarily derived from biomass gasification, are typically catalytically hydrogenated to produce methanol according to the following main reactions:

(1)

(2)

(3)

According to Eqs (1)-(3), methanol production is an exothermic process that occurs with a significant mole reduction according to several potential kinetic models (Leonzio, 2020). Thus, methanol production is thermodynamically favoured by high pressure (50-100 bars) and temperature below 300°C (Sarvestani et al., 2024). Moreover, the exothermic nature of methanol synthesis requires efficient heat removal to prevent catalyst deactivation and by-product formation. Due to their high selectivity and activity, copper-based catalysts are commonly used in industrial applications. Supporting materials such as silica, alumina, and zirconia enhance thermal stability and catalyst dispersion, while zinc oxide (ZnO) helps protect copper from contaminants and mitigates the acidic nature of alumina, reducing the formation of dimethyl ether (Sarvestani et al., 2024). Gas-phase reactors with precise temperature control are primarily used to produce methanol. Typically, fixed-bed reactors operate under adiabatic conditions with multiple reactors connected in series and intermediate cooling to recover heat (Mancusi et al., 2021). The isothermal reactors developed by Linde offer better temperature control and lower conversion efficiency per pass, necessitating high recycling rates. Despite their superior temperature control, liquid-phase reactors are less common due to scaling and modelling challenges, although they are preferred when gas feeds have a high hydrogen-to-carbon ratio. In recent years, zeolite and ceramic membrane reactors have been developed, which reduce capital and operating costs by removing methanol and water during the reaction, thereby increasing methanol yield.

Overall, this work aims to develop a novel co-generative technology to produce methanol through bio-syngas from waste biomass. For this purpose, residual biomasses in southern Italy will be selected and characterized for their use in syngas production for methanol synthesis. A non-stoichiometric method based on Gibbs free energy minimization was used to simulate biomass gasification for syngas production with steam as a gasifying agent and subsequent syngas adjustment through WGS reaction. The produced syngas are fed to a methanol reactor. We want to propose a methanol reactor configuration consisting of a membrane for water separation, an electrolyzer splitting the water produced by methanol synthesis and a heat exchanger for heat recovery integrated into one equipment. This reactor studies methanol production for different biomasses under the gasification process.

* 1. Biomass characterization and syngas production

To assess the potential availability of biomass and by-products in southern Italy, a preliminary analysis has been performed using the WebGis ENEA portal “Atlante delle Biomasse” (Pierro et al., 2021).  Generally, many miscellaneous biomass types exist whose gasification leads to a wide range of gas stream composition. To consider this context with a good approximation, we used several heterogeneous biomasses as feed for gasification. Such a variety of gasification feed for simulation ensures that actual experimental data are well described. Based on an average of the trends from 2013-2023, cereal straw (3850 kt/y), pruning waste (2200 kt/y) and grape marc (880 kt/y) were found to be the three most commonly available biomass types. Due to the heterogeneous nature of pruning waste, we focused our research solely on cereal straw and grape marc waste. Considering the importance of the agri-food sector in southern Italy, particularly tomato production, tomato peel biomass was selected. Almost all tomato processing industries are in south Italy, and tomato peels are an important by-product. In the Campania agri-food sector, tomato cultivation accounts for 30% of regional food production and 15% of national horticulture production (Di Fraia et al., 2020). The proximate and ultimate analyses of the selected type of biomass have been carried out according to ASTM D5142 and ASTM D5373 procedures. The proximate analysis provided the percentages of volatile matter, fixed carbon, and inorganics (ash). In contrast, the ultimate analysis has given an insight into the elemental composition of the considered biomass in terms of C, H and N. The ultimate analysis of the samples was carried out using a LECO CHN 628 (ASTM D5373) for the determination of C, H, and N content), whereas the proximate analysis was performed by means of a LECO TG701 according to ASTM D5142 for the evaluation of moisture, volatile matter, ash, and fixed carbon contents.

Table 1: Proximate analysis (as received), ultimate analysis (on dry basis), and HHV experimental results.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Cereal straw | Grape marc | Tomato peels |
| Moisture | 65.14 | 13.25 | 80.5 |
| Fixed Carbon | 8.89 | 20.87 | 2.28 |
| Volatiles | 9.50 | 62.58 | 16.87 |
| Ash | 16.47 | 3.31 | 0.35 |
| C | 38.07 | 41.82 | 58.3 |
| H | 7.27 | 6.18 | 7.72 |
| N | 0.3 | 0 | 1.49 |
| HHVdb kJ/kg | 16379 | 16942 | 25820 |

Experimental results are reported in Table 1 Higher Heating Value on dry basis (HHV), carried out using a PARR 6200 Isoperibol Oxygen Bomb Calorimeter. Biomass is converted into syngas through the gasification process, which is modelled under equilibrium conditions. Mathematical models based on thermodynamic equilibrium accurately predict the maximum yield of a desired product within a reacting system, providing an upper limit of its composition. They are unaffected by specific gasifier designs, so only fuel and process parameters can be considered. Two different approaches can be pursued in equilibrium modelling (Patra and Sheth, 2015), namely the stoichiometric and non-stoichiometric methods. In the first case, a detailed specification of all the chemical reactions and species involved in the model is required. At the same time, the non-stoichiometric method is based on Gibbs free energy minimization. By minimizing Gibbs free energy, the concentration values at equilibrium of all reactive species, both products and reactants, can be evaluated using a general mathematical technique, even if the kinetic pathway is unknown. The non-stoichiometric method has been used to model the gasification process and water gas shift reactor. The outcoming gas composition has been calculated considering that Gibbs energy, accounting for condensed and non-reacting species, reaches its minimum value at chemical equilibrium. The total Gibbs energy is given by:

(4)

The problem is finding the set *ni* that minimizes *Gt* for given values of pressure and temperature, subject to the constraints of the material balances. The material balance on each element *k* may be written assuming that the total number of atoms of each element is constant:

(5)

In Eq. (5), Ak is the total number of atomic masses of the kth element (according to ultimate analysis C, H, O, N, S) in the system, as determined by the initial constitution of the system; is the number of atoms of the kth element present in each molecule of chemical species *i*. The Gibbs energy for these species is calculated from the Gibbs-Helmholtz relation:

(6)

Enthalpy and entropy in Eq. (6) have been calculated by the NIST WebBook formulas and coefficients (Linstrom and Mallard, 2014). The gasification product for several temperatures and S/B feed ratios is reported for the three analysed biomass in Fig. 1.

Immagine che contiene diagramma, linea, testo, Diagramma

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*Figure 1: Effect of gasification temperature and S/B ratio on H2/CO molar ratio for: (a) Cereal straw; (b) grape marc; (c) tomato peels.*

As biomass gasification temperature increases, the H2/CO ratio decreases. In the explored gasification temperature range, the Boudouard reaction () predominated over the water gas reaction (C. Thus, increasing gasification temperature led to increased CO concentration, whereas H2 concentration remained relatively constant. With an increasing S/B ratio, steam is added to the feed, enhancing the water gas and steam methane reforming reactions, which increase CO and H2 concentrations. The benefits of high gasification temperatures include a greater production of gaseous products and an improved degree of tar reduction, especially without catalysts. However, they also significantly impact the equipment cost as the temperature rises above 900°C (Thomson et al., 2020). Moreover, feeding only a low amount of steam is advantageous because producing steam is energy-intensive (Thomson et al., 2020). The gas composition for a gasification temperature of 900°C and S/B equal 2 are reported in Table 2.

Table 2: Gas composition percentage on dry basis for a gasification temperature of 900°C and S/B=0.2

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Feedstock | H2 | CO | CO2 | CH4 | N2 | H2/CO |
| Cereal straw | 53.81 | 23.91 | 22.0 | 0.13 | 0.17 | 2.25 |
| Grape marc | 54.82 | 32.92 | 12.3 | 0.2 | 0 | 1.67 |
| Tomato peels | 52.07 | 27.47 | 5.88 | 0.03 | 0.037 | 1.95 |

According to Table 2, the H2/CO ratio of the syngas produced ranges between 1.67 and 2.25. A syngas feed is usually required for methanol production with an H2/CO ratio of 2. Thus, the H2/CO ratio must be adjusted close to this ratio. Water gas shift (WGS) reaction or Reverse Water Gas Shit (RWGS) (Eq.3) can be used for the adjustment of H2/CO ratio. Temperatures between 250 and 400 °C are conducive to the exothermic WGS reaction, while temperatures above 400 °C are conducive to RWGS.

In Fig. (2), the effect of operating temperature and S/B feed ratio for the three feedstocks considered is reported; the dashed line represents the best couple of temperatures and S/B to ensure an H2/CO ratio close to 2.

Immagine che contiene testo, schermata, Policromia, Diagramma

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*Figure 2: Effect of gasification temperature and S/B ratio on H2/CO molar ratio for: (a) Cereal straw; (b) grape marc; (c) tomato peels.*

* 1. Preliminary modelling and simulation of membrane reactor for methanol production

The syngas compositions reported in Table 2 were used as feed to a catalytic zeolite-membrane reactor as a preliminary test to produce methanol. Mass, energy and momentum balances on tube and shell side of the reactor are reported in the following expressions, where the dependent variables of the system – *xi, T* and *P* – are represented by the compositions of the reaction stream, the temperature and the pressure. The coefficients *xi*, *T* and *P* arise from the Peng-Robinson EoS applied to a mixture of non-ideal gases

a) Mass balances on both tube and shell side

 (7)

b) Energy balances on both tube and shell side

 (8)

c) Momentum balance on the tube side

 (9)

d) Momentum balance on the shell side

 (10)

* 1. Preliminary results and discussion

The figures below show the reaction side composition and temperature profiles for syngas from cereal straw biomass. The results related to grape marc and tomato peels are similar and, thus, are not shown.



Figure 3: Composition and temperature profiles along the reactor using syngas feed from cereal straw at a feed temperature of 220°C.

Table 3: Composition and reactor outlet temperature for different temperatures and feed conditions using syngas from cereal straw gasification.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Cereal straw | | *Inlet temperature [°C]* | | |
| Species | *Feed [%]* | *220* | *240* | *260* |
| *Outlet composition [%]* | | |
| CO | 23.91 | 23.40 | 23.74 | 24.07 |
| CO2​ | 22.00 | 22.24 | 21.94 | 21.65 |
| H2 | 53.81 | 49.59 | 49.97 | 50.32 |
| H2O​​ | 0.00 | 1.20 | 1.28 | 1.36 |
| MeOH | 0.00 | 3.27 | 2.77 | 2.30 |
| Inert | 0.28 | 0.30 | 0.30 | 0.29 |
| Inlet velocity [m/s] = 0.5 | P [bar] = 50, Tout  [°C] = | 299.2 | 304.7 | 310.8 |

Table 4: Composition and reactor outlet temperature for different temperatures and feed conditions using syngas from grape marc gasification.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Grape marc | | *Inlet temperature [°C]* | | |
| Species | *220* | *220* | *240* | *260* |
| *Outlet composition [%]* | | |
| CO | 32.72 | 32.19 | 32.40 | 32.60 |
| CO2​ | 12.30 | 12.51 | 12.35 | 12.19 |
| H2 | 54.82 | 51.27 | 51.68 | 52.05 |
| H2O​​ | 0.00 | 0.59 | 0.63 | 0.68 |
| MeOH | 0.00 | 3.27 | 2.77 | 2.31 |
| Inert | 0.16 | 0.17 | 0.17 | 0.17 |
| Inlet velocity [m/s] = 0.5 | P [bar] = 50, Tout  [°C] = | 310.1 | 315.5 | 321.6 |

In Figure 3, it can be observed that, at the feeding conditions used, thermodynamic equilibrium conditions are reached. Tables 3 and 4 report the output composition values ​​for each feed temperature considered in the simulations. It is possible to see how the methanol content at the outlet is quite low, implying that the feeding conditions - i.e., composition and temperature of syngas - and the membrane performance- must be optimized to maximize the methanol yield. Furthermore, a single-stage reactor is considered. These factors will be assessed in a future work.

* 1. Conclusions

In this paper, a preliminary study on methanol production from syngas of different compositions obtained from the gasification of several types of biomasses was conducted. In particular, three types of residual biomass from southern Italy were selected and characterized by proximate and ultimate analyses to feed them to gasification for syngas production, which was considered feed for methanol synthesis in a zeolite-membrane reactor. A non-stoichiometric method based on Gibbs free energy minimization was used to simulate biomass gasification for syngas production. The membrane reactor was modelled by a first-order model considering the mass, energy and momentum variation along the axial direction on both feed and permeate sides. The preliminary results showed that the syngas inlet conditions are not satisfactory to lead to an acceptable methanol yield. Therefore, different staged configurations are required for the purpose.

Nomenclature

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *db* | dry base | *u* | Velocity, m s-1 | *U* | Heat transfer coefficient, W m-2 K-1 |
| *nt* | Number of membranes | *z* | Axial abscissa, m | *M* | Molecular weight, mol kg-1 |
| *P* | Pressure, bar | *C* | Concentration, mol m-3 | *J* | Transmembrane molar flux, mol m-2 s-1 |
| *S/B* | Steam/Biomass ratio | *T* | EoS factor for temperature | ** | Density, kg m-3 |
| *T* | Temperature, K | *P* | EoS factor for pressure | *ID, OD* | Inner and Outer Diameter |
| *x, y* | Molar fractions | *Ac* | Cross-sectional area, m2 | *fE* | Ergun friction coefficient |
| H | Enthalpy, J mol-1 | *tb, sh* | Tube and Shell | *fF* | Fanning friction coefficient |

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References

Di Fraia S., Fabozzi S., Macaluso A., Vanoli L., 2020, Energy potential of residual biomass from agro-industry in a Mediterranean region of southern Italy (Campania), J. Clean. Prod., 277, 124085.

Gautam P., Nehaa S., Upadhyayb S.N., Dubey S.K., 2020, Bio-methanol as a renewable fuel from waste biomass: Current trends and future perspective. Fuel, 273, 117783.

Kafrudi G. E., Samiee L., Mansourpour Z., Rostami T., 2022, Optimization of methanol production process from carbon dioxide hydrogenation in order to reduce recycle flow and energy consumption. J. Clean. Prod., 376, 134184.

Leonzio, G., 2020. Mathematical modeling of a methanol reactor by using different kinetic models, J. Ind. Eng. Chem. 85, 130-140.

Linstrom P.J., Mallard WG. NIST Chemistry webBook, NIST standard reference database number 69. Natl Inst Stand Technol; 2014. citeulike-article-id:3211271.

Mancusi E., Bareschino P., Brachi P., Coppola A., Rupppolo G., Urciuolo M., Pepe F., 2021, Feasibility of an integrated biomass-based CLC combustion and a renewable-energy-based methanol production systems, Renew. Energy, 179, 29-36.

Moosmann L., Siemons A., Fallasch F., Schneider L., Urrutia C., Wissner N., Mendelevitch, R., Hermann, H., Healy, S., Oppelt, D., & Heinemann, S., 2022, The COP27 Climate Change Conference Status of climate negotiations and issues at stake Policy Department for Economic, Scientific and Quality of Life Policies Directorate-General for Internal Policies. European Union.

Patra T. K., Sheth P, N., 2015, Biomass gasification models for downdraft gasifier: A state-of-the-art review. Renew. Sustain. Energy. Rev., 50, 583–93.

Pierro N., Giocoli A., Motola V., Dipinto S., 2021. Valutazione disponibilità biomasse agro-industriali a livello nazionale e loro pubblicazione sul portale Webgis atlante delle biomasse, [https://hdl.handle.net/20.500. 12079/56881](https://hdl.handle.net/20.500.12079/56881)

Sarvestani M.E., Norouzi O., Di Maria F., Dutta A., 2024, From catalyst development to reactor Design: A comprehensive review of methanol synthesis techniques, Energ. Convers. Manage., 302, 118070.

Thomson R., Kwonga P., Ahmad E., Nigam K.D.P. , 2020, Clean syngas from small commercial biomass gasifiers; a review of gasifier development, recent advances and performance evaluation, Int. J. Hydrogen Energ., 45, 21087-21111