



The 8th International Conference on Applied Energy – ICAE2016

Low Impact Methanol Production from Sulfur Rich Coal Gasification

Andrea Bassani^a, Giulia Bozzano^a, Carlo Pirola^b, Eliseo Ranzi^a, Sauro Pierucci^a, Flavio Manenti^{a*}

^aPolitecnico di Milano – Dipartimento CMIC “Giulio Natta” Piazza Leonardo da Vinci 32, 20133 Milano, Italy

^bUniversità degli Studi di Milano – Dipartimento di Chimica Via Golgi 19, 20133 Milano, Italy

Abstract

In economy nowadays, methanol is already a key compound widely employed as building block for producing intermediates or synthetic hydrocarbons, solvent, energy storage medium, and fuel. In recent times, methanol has been employed in a number of innovative applications. It is a clean and sustainable energy resource that can be produced starting from different sources traditional or renewable: natural gas, coal, biomass, landfill gas and power plant/industrial emissions. In this work is proposed an innovative low impact process for methanol production starting from coal gasification. The most important features, instead the traditional ones, are the lower emissions of CO₂ (about 2.5 %) and the surplus production of methanol (about 1.7%) without any addition of primary sources. Moreover, it is demonstrated that a coal charges with a high sulfur content means a higher reduction of CO₂ emissions. The key idea is the application of AG2STM technology that is a completely new effective route of processing acid gases: H₂S and CO₂ are converted into syngas (CO and H₂) by means of a regenerative thermal reactor.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Keywords: CO₂ reuse; Methanol synthesis, Improved coal gasification; Syngas from emissions.

1. Introduction

Nowadays, methanol is used as primary feedstock for a large variety of chemicals. Among the most important, we can mention formaldehyde [1], methyl-tert-butyl ether (MTBE, 20%), acetic acid and dimethyl ether [2]. Methanol is also used as transportation fuel in addition to gasoline and, in the future, it

* Corresponding author. Tel.: +39 (0)2 2399 3273; fax: +39 (0)2 2399 3280.
E-mail address: f.lavio.manenti@polimi.it

will certainly play an increasing role in such field. The traditional production pathway via synthesis gas [3]. Other than methanol could be manufactured in different and new ways. The carbon source may be natural gas or CO₂, which can be recovered from industrial sites and, eventually, from the atmosphere. This second production pathway would allow mitigating global warming due to the increasing presence of greenhouse gases in the atmosphere. All energy sources can be exploited for methanol production, thus the “Methanol Economy” [4] offers a feasible means of using and storing all sources of energy (renewable, atomic, etc.). Another interesting source of carbon could be the coal charges due to their relatively low cost, widespread availability and distribution, plus the fact that they are less vulnerable to political constraints. That said, coal is a cause of environmental concern and not only because of the greenhouse effects resulting from the CO₂ emissions. Indeed, hydrogen sulfide is a common byproduct in coal gasification process and the strict legislation that limits its release into the atmosphere have triggered renewed interest in the modeling of sulfur chemistry [5]. The most important and spread neutralization method is based on the Claus process [6]. Basing on recent advances [7], it could be also possible to convert H₂S and CO₂ into valuable products and specifically into syngas according to the oxi-reduction reaction:



The target of this study is to demonstrate that higher content in sulfur means both lower emissions of CO₂ (without any additional environmental impact due to organosulfur species) and a surplus production of methanol without any addition of primary sources.

Nomenclature

MDEA	Methyl DiEthanolAmine
RTR	Rigenerative Thermal Reactor
TMP	Traditional Methanol Process
NMP	Novel Methanol Process

2. Process Description

In this paragraph, the overall layout of the novel methanol production process is discussed and then each part is analyzed. For each section, some numerical results are presented comparing the simulation of the traditional process with the new in order to prove the validity and highlighting the possible advantages and disadvantages. A spread and commercial process simulation software (Aspen HYSYS®, by AspenTech), is used for this simulation excepting the coal gasifier that is simulated using GASDS [8]. The Peng-Robinson equation of state is used for the entire process except for the amine wash section, where the amine package included in Aspen HYSYS® is adopted. The Figure 1 shows a simplified BFD of the traditional methanol synthesis from coal gasification and the novel process.

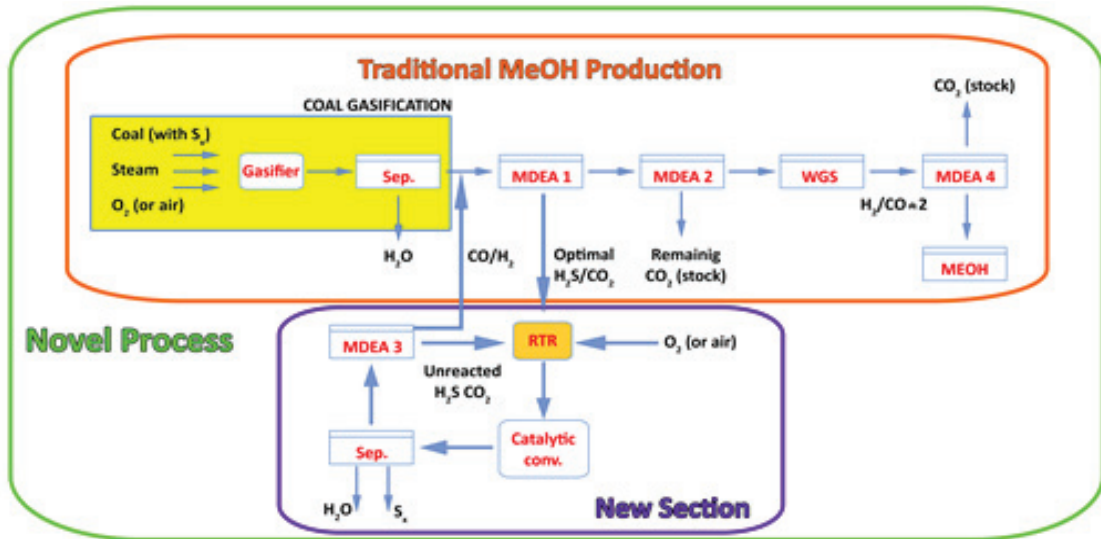


Figure 1 Process Layout of traditional and novel methanol production process

2.1. Coal Gasification

In this work, Chinese coal [9] was chosen as a possible feedstock for the plant. The ultimate analyses of the considered fuel shows a high sulfur content (about 9% wt) which is in good agreement with the target of the paper. Coal gasifier is simulated using a multi-scale, multi-phase, and multi-component model which describe coal gasification system by means of detailed kinetic mechanisms for coal pyrolysis, char heterogeneous reactions and for successive gas-phase reactions [10]. These kinetic mechanisms are then coupled with transport resistances resulting in first-principles dynamic modeling of non-ideal reactors of different types (e.g., downdraft, updraft, traveling grate), also including the catalytic effect of ashes. Figure 2 summarizes the inlet coal charge and the outlet syngas composition.

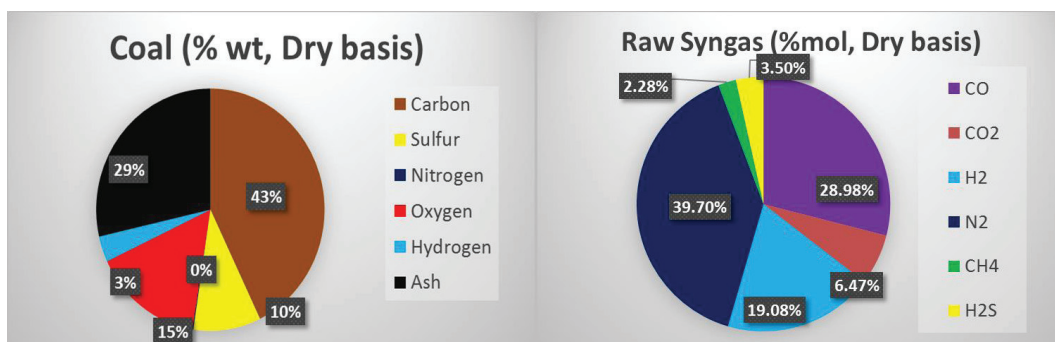


Figure 2 Inlet coal charge ultimate analysis and outlet raw syngas composition

2.2. Amine Section

The syngas must be purified from acid gases (H_2S and CO_2). For this work is decided to use an amine wash, using MDEA that is chosen for its industrial application and its specific selectivity to hydrogen sulfide, that allow to control the ration between H_2S and CO_2 that is crucial in this process. For instance, the first amine wash aims to remove almost all of the H_2S from the acid gas stream. Simultaneously is limited the absorption of CO_2 , that is the main source of CO and at the same time a "heat absorber" in the furnace. If there is an excess of CO_2 , more oxygen should be required to reach the desired temperature, leading to a major consumption of H_2S for oxidation instead of consumption of H_2S for pyrolysis.

2.3. Acid Gas To Syngas™ (AG2S™) technology

The acid gas stream coming from sweetening section is sent to the AG2S™ process [7]. The core of the plant is RTR, which has a different configuration compared with the typical Claus furnace. RTR design allows to produce a greater amount of H_2 . The key idea is to feed an optimal ratio of H_2S and CO_2 and to preheat the inlet acid gas before the combustion. Hydrogen is produced almost all by the H_2S pyrolysis. Therefore, if the temperature of the acid gases, for instance, rises up to about $700^\circ C$ in AC-1, and then to about $1100^\circ C$ in the furnace before the combustion, the oxygen flow rate required to reach the standard temperatures in the furnace (1100 - $1350^\circ C$), is much lower than the typical oxygen provided for the Claus processes and the H_2S potential for pyrolysis is completely exploited. It is important to emphasize that the reactor is simulated using DSMOKE (software for ideal reactor simulation with a detailed kinetic scheme), which is integrated within Aspen HYSYS® with the use of Visual Basic programming language. This allows to integrate a detailed kinetic scheme [11], within non-ideal reactor models and in turn into commercial environments for the simulation of chemical plants. The catalytic reactor configuration is the typical one of the Claus process, but the reactions involved are mainly the hydrolysis of CS_2 and COS. The simulation of the catalytic reactor is carried out using conversion reactor in Aspen HYSYS®. The typical conversion of hydrolysis reaction is about 75% on alumina catalyst [12] and of about 100% for Claus reaction. The inlet od outlet stream of this section with the related compositions are reported in Table 1.

Table 1 Inlet and outlet streams of AG2S process section

	Flow rate [kmoli/h]	x_{mol} H_2S	x_{mol} CO_2	x_{mol} H_2	x_{mol} CO	x_{mol} H_2O	x_{mol} CH_4
Acid Gas Form "MDEA 1" (NMP)	70.09	0.256	0.674	-	-	0.070	-
Syngas from "MDEA 3" (NMP)	6.49	-	-	0.175	0.823	-	-

2.4. Methanol process

Methanol synthesis is simulated using simplified kinetic mechanism and reactor models already included in Aspen Hysys [13] as reported in Figure 3. Reaction is performed on a copper/zinc oxide

catalyst supported on aluminum oxide [14]. Equations (2) and (3) show the possible conversion routes of syngas into methanol:



The synthesis reaction was modelled with the aid of the rate equations supplied by Graaf et al. [15]

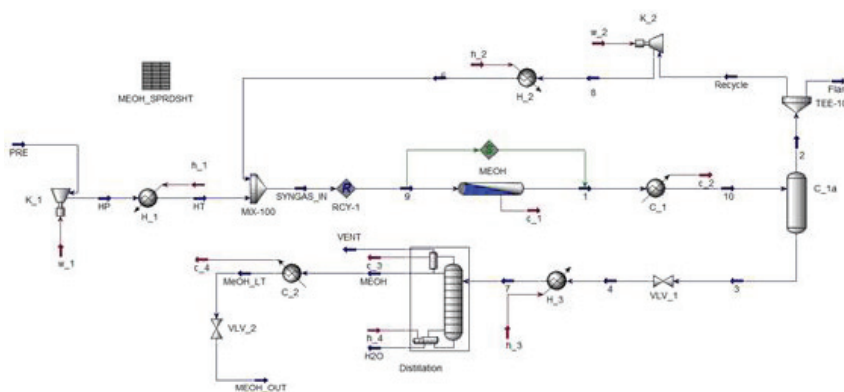


Figure 3 Aspen Hysys MeOH synthesis flowsheet

3. Results and Discussion

Table 2 reports the comparison between the two processes in terms of syngas, CO₂ and methanol production. It is important to underline the fact that there is an uncertainty in the results due to the detailed kinetics used for the furnace simulation. Indeed, the prediction of H₂S pyrolysis is not too accurate [11] and so an error of about 5% is present in the system. The overall amount of methanol is increased of ~1.7 %. This is due to the fact that AG2STM technology allows not only to convert a certain amount of CO₂ but also to produce an additional amount of syngas. Indeed, AG2STM technology reduces the amount of CO₂ by ~2.4% and the additional amount of syngas is equal to ~1.7% compared to the traditional coal gasification process.

Table 2 NMP compered to TMP

	TMP	NMP
Syngas Production [kmol/h]	382.17	388.54
CO ₂ emissions [kmol/h]	119.38	116.49
MeOH Production [kmol/h]	178.76	181.78

4. Conclusions

In this work is presented a novel process for industrial methanol production that allow to increase the outlet stream flowrate without using any additional primary sources with low environmental impact. The idea is to reduce the emissions of H₂S and CO₂ and, at the same time, to exploit the oxidizing capacity of

CO₂ with H₂S to ease the recovery of syngas, which is the base for methanol production. Given the innovative nature of the process, this technology requires more detailed analysis before it can be used on a real industrial plant, but this highlights that the novel process is very interesting and economically appealing.

References

- [1] Koivikko N., Laitinen T., Ojala S., Pitkääho S., Kucherov A., Keiski, R. L.. Formaldehyde production from methanol and methyl mercaptan over titania and vanadia based catalysts. *Applied Catalysis B: Environmental* 2011; 103(1), 72-78.
- [2] Ng K. L., Chadwick D., Toseland B. A. Kinetics and modelling of dimethyl ether synthesis from synthesis gas. *Chemical Engineering Science* 1999, 54, (15-16), 3587-3592.
- [3] Cai Y., Niu Y., Chen Z. Synthesis of methanol and isobutanol from syngas over ZrO₂-based catalysts. *Fuel processing technology* 1997, 50(2), 163-170.
- [4] Bozzano G., Manenti F. Efficient methanol synthesis: Perspectives, technologies and optimization strategies. *Progress in Energy and Combustion Science* 2016: 56, 71–105.
- [5] Maffei T., Sommariva S., Ranzi E., Faravelli T. A predictive kinetic model of sulfur release from coal. *Fuel* 2012, 91(1), 213-223.
- [6] Pierucci S., Ranzi E., Molinari L. Modeling a claus process reaction furnace via a radical kinetic scheme. *Computer Aided Chemical Engineering* 2004, 18, 463-468.
- [7] Bassani A., Pirola C., Maggio E., Pettinau A., Frau C., Bozzano G., et al. Acid Gas to Syngas (AG2S™) technology applied to solid fuels gasification: a new way to reduce H₂S and CO₂ emissions by improving Syngas production. *Appl Energy* 2016; doi:10.1016/j.apenergy.2016.06.040.
- [8] Cabianca L., Bassani A., Amaral A.F., Rossi F., Bozzano G., Ranzi E., et al. GASDS: a Kinetic-Based Package for Biomass and Coal Gasification. *Chemical Engineering Transactions* 2016: 50, pp. 247-252.
- [9] Xie P., Song H., Wei J., Li Q. Mineralogical Characteristics of Late Permian Coals from the Yueliangtian Coal Mine, Guizhou, Southwestern China. *Minerals* 2016, 6(2), 29.
- [10] Corbetta M., Bassani A., Manenti F., Pirola C., Maggio E., Pettinau A., et al. Multi-scale Kinetic Modeling and Experimental Investigation of Syngas Production from Coal Gasification in Updraft Gasifiers. *Energy&Fuels* 2015, 29, 3972–3984
- [11] Manenti F., Papisidero D., Frassoldati A., Bozzano G., Pierucci S., Ranzi E. “Multi-scale modeling of Claus thermal furnace and waste heat boiler using detailed kinetics”. *Computers & Chemical Engineering* 2013, 59, 219-225.
- [12] Rhodes C., Riddell S.A., West J. B., Williams B.P., Hutchings G.T. The low-temperature hydrolysis of carbonyl sulfide and carbon disulfide: a review. *Catalysis Today* 2000, 59(3), 443-464.
- [13] Pellegrini L. A., Soave G., Gamba S., Langè S. Economic analysis of a combined energy–methanol production plant. *Applied energy* 2011, 88(12), 4891-4897.
- [14] Manenti F., Leon-Garzon A.R., Bozzano G. Energy-process integration of the gas-cooled / water- cooled fixed-bed reactor network for methanol synthesis. *Chem. Eng. Trans.* 2013, vol. 35, pp. 1243–1248.
- [15] Graaf G.H., Stadhuis E. J., Beenackers A. A. C. M. Kinetics of low-pressure methanol synthesis. *Chem. Eng. Sci.* 1988, vol. 43, no. 12, pp. 3185–3195.



Biography

Andrea Bassani was born in Lecco in June 1989. In 2014, he graduated in Chemical Engineering at Politecnico di Milano. Then he started the PhD School in Industrial Chemistry and Chemical Engineering at Politecnico di Milano, addressing the multiscale model and simulation using different tools like Aspen Hysys, Matlab, c++.