

Process Optimization of Hydrogen Production from Coal Gasification

E. Biagini¹, G. Pannocchia², M. Zanobini², G. Gigliucci³, I. Riccardi³, F. Donatini³, L. Tognotti²

1. Consorzio Pisa Ricerche – Divisione Energia e Ambiente – Italy

2. Dipartimento di Ingegneria Chimica – Università di Pisa – Italy

3. Enel Produzione Ricerca – Pisa – Italy

1. Introduction

Hydrogen is a high quality energy carrier, contains no carbon and generates little or no polluting emissions at the point of use. A hydrogen-based energy system is an advantageous option for delivering efficient, clean and safe energy in a wide range of applications [1]. At present, significant cost and performance improvements in production, storage, transportation and technologies are required. Research, development and commercial efforts should be combined to achieve these goals.

Hydrogen is a secondary form of energy, produced using other primary energy sources. Most of the hydrogen is made by steam reforming of natural gas (which is mainly methane). However, the use of coal as source is desirable, being a low-cost fuel and guaranteeing a long-term availability. Coal gasification is an efficient, clean and versatile process, which can be adapted for producing hydrogen [2]. The comparison of different technologies as well as the assessment of advanced options (e.g. introduction of a combined cycle, use of pure oxygen, CO₂ sequestration) are necessary to maximize the conversion, the process efficiency and the environmental benefits [3]. Even, the integration of the gasification process with a centralized power plant (thus sharing steam, heat, emissions and residue char) may be competitive, reducing significantly the cost for hydrogen production.

This work aims to assess the efficiency of the coal gasification process, the opportunity of different options and the effect of the operating conditions on hydrogen production, net energy production. Preliminary experimental applications and process modeling on the coal pyrolysis Enel plant of Bastardo (Perugia – Italy) gave promising results [4]. These are the bases to develop a process optimization method, which uses thermodynamic databases, parametric models (for the pyrolysis and gasification steps) and a steady state simulation software. The results reported in this work are a first example of the potential of combining these tools and will be deepened in the frame of the FISIR project “Integrated Systems for Hydrogen Production and Use in Distributed Generation”, which will optimize the integration with a centralized power plant [5].

2. Process description, boundary definition and method development.

The process is thought into a centralized power plant. Therefore, coal feedstock and lines are out of the process boundary as well as exhaust gas treatment units. The process is formed by the interconnection of 4 macro-units: coal gasification, gas clean-up/heat recovery, water gas shift reaction, hydrogen separation. Steam generation, final syngas combustion and turbines are considered for evaluating the efficiency of the combined cycle. The steady-state simulation software AspenPlusTM is used to model each block, to link different options and to perform the sensitivity analysis varying the operating conditions. The performance parameters of each single block (e.g. turbine efficiency, steam temperature) and the operating range are typical of power plants and are adopted from direct measurements and literature works. In particular, different gasification options are considered (Figure 1):

- direct gasification (DG), performed in a single reactor, where coal, steam and pure oxygen (from a dedicated air separation unit) are fed in different points; partial combustion of the coal provides the heat necessary for the gasification;
- indirect gasification (IG), coupling a gasification reactor (fed with coal, steam and a heat vector, e.g. sand in a circulating bed reactor) with a combustor (where the sand is heated by the combustion of the unreacted char with air and recycled to the gasification); alternatively, the char may be burnt in the centralized furnace, which assures the highest efficiency, while steam and heat necessary for the gasification may derive from appropriate lines in the centralized power plant.

The CO₂ sequestration unit is not considered in this work because data on technological feasibility lack at present. However, this is a fundamental option for improving the worth of the process and gain further environmental benefits [6]. A future work will consider this unit taking into account the present method and the obtained results.

Both options are modeled in AspenPlusTM procedures, which are described in the next section, giving actually more details for the gasification unit. The units are linked (with material streams, heat and energy exchange) to give different scenarios in section 4, where the results of the sensitivity stream analysis as well as the comparison of the targets are discussed for the most significant cases. In particular, the main targets are:

- hydrogen production efficiency $\eta_H = \frac{H_2 \text{ produced (kg / s)} * HV \text{ of hydrogen (kJ / kg)}}{\text{coal fed (kg / s)} * HV \text{ of coal (kJ / kg)}}$
- net power efficiency $\eta_P = \frac{\text{net power (kW)}}{\text{coal fed (kg / s)} * HV \text{ of coal (kJ / kg)}}$

Other operating parameters (i.e. imposed before every simulation) as well as monitoring parameters (i.e. calculated values of interest) are defined in the next section to describe synthetically and precisely the entire process and to allow the comparison of different cases.

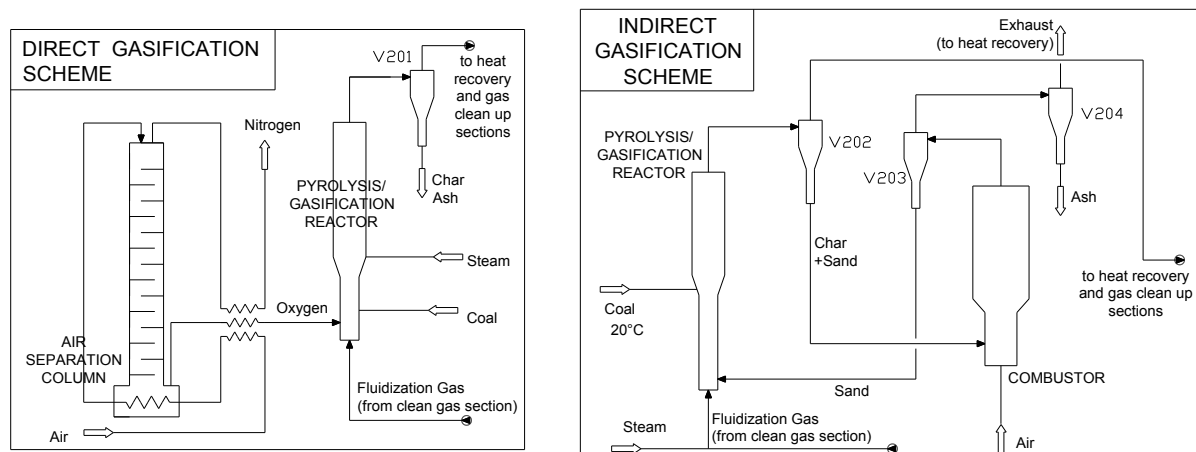


Fig. 1. Process gasification options.

3. Flowsheet modeling

3.1. Pyrolysis/gasification model

The pyrolysis model is common to both gasification configurations. The formation of pyrolysis products (volatiles, char and ash) is supposed to be complete in every conditions (the temperature of the reactor is never under 1000 °C) in a negligible time respect to the gasification reactions. Volatile speciation is calculated according to the results of a modified version of the CPD model (Chemical Percolation Devolatilization [7]). The original version

of the CPD model provides the conversion in light gases (CO , CO_2 , H_2O , CH_4) and other no specified gases. Coupling this approach with material and elemental balances under specific assumptions (tar composition: C 85%, H 4%, O 5%, others 6%; sulfur and nitrogen released as H_2S and HCN , respectively), conversion in light hydrocarbons and hydrogen can be calculated as function of the initial composition of the coal and the pyrolysis temperature. The pyrolysis model is connected to the gasification model according to the specific configuration. In the direct gasification scheme, pure oxygen (from the air separation unit) and pyrolysis products are fed at the same level. The C/O ratio (coal to oxygen ratio, on a mass basis) is an operating parameter to determine the temperature of the gasifier. Steam is supposed to be fed (in the operating parameter C/S, coal to steam ratio) to start the gasification reactions, once the partial combustion consumed all oxygen. No reactions are specified in the model, a Gibbs free energy minimization is actually performed considering all the species (also the char as graphite) in the equilibrium conditions (of pressure and temperature).

In the indirect gasification, a dedicated combustor (fed with the sand and the unreacted char) provides the heat necessary to the gasifier. Pyrolysis products and steam (in the C/S ratio) react to give the minimum of the Gibbs free energy in the actual conditions. In both configurations, the hydrogen concentration after the gasification step is monitored, as well as the temperature of gasification (T_G), which depends on the heat generated or recycled, the imposed C/S and C/O ratios.

The opportunity to consider the equilibrium of gasification is verified simulating the gasification of a single particle in a self developed parametric model [4]. At $1200\text{ }^\circ\text{C}$, the gasification is practically complete (95% of the equilibrium) after 6 s, considering only H_2O as gasifying agent (in the concentration of the present study). This value is low enough to be practically achieved in a circulating or entrained flow reactor.

3.2. Gas clean up and heat recovery section

In both configurations, this section is schematized as a series of operations:

- a first partial quench, which decreases dramatically the temperature of the gas (from approximately $1200\text{ }^\circ\text{C}$ to a fixed temperature of $800\text{ }^\circ\text{C}$), thus allowing the practical introduction of heat exchangers;
- a series of heat exchangers, which produces steam of different quality for a dedicated steam cycle (formed by steam turbine, condenser and pumps) contributing to the net power generated in the process (or alternatively can give additional steam in the centralized plant) and reduces the temperature of the gas to approximately $250\text{ }^\circ\text{C}$;
- a high temperature filtration unit, eliminating the ash;
- a sulfur removal unit;
- a heat recovery, to achieve the desired temperature for the water gas shift reaction (T_W), which is a monitored parameter.

3.3. Water gas shift reaction section.

The water gas shift reaction is an exothermic reaction. It is favored by low temperature and the catalyst used (CoMo as in the Topsoe process [3] or FeCr/CuZn [8]) is assumed to bring the gas to equilibrium. It is schematized in two fixed bed reactors operating at high temperature (T_{WH} approximately $450\text{ }^\circ\text{C}$), and low temperature (T_{WL} approximately $280\text{ }^\circ\text{C}$), respectively. An intermediate heat exchanger allows the temperature of the gas to be reduced.

3.4. Hydrogen separation unit

Hydrogen separation is performed in a pressure swing adsorption (PSA) unit. It is assumed to give high purity H_2 (99.999%) with an efficiency of 85%. The exit gas contains CO_2 , CO , H_2 and a small amount of other species. The heating value is generally high enough to be burned, providing a net power using a gas turbine or alternatively can be burned in the centralized plant to give additional energy input.

4. Results and discussion

In this work the results of the stream sensitivity analysis of both configurations are reported. A common flowsheet is schematized in Figure 2. A high sulfur coal is used (Table 1). The potentiality of the plant is fixed as a part of the centralized power plant (10% of the produced power). Therefore, the inlet flowrate of the coal can be fixed (20000 kg/h).

The operating parameters are the ratios C/S and C/O for the DG configuration, C/S and the heat from the combustor for the IG configuration. In all cases, the reference value of C/S is 1.92. The reference C/O value for DG (1.24) and the heat from the combustor in the reference conditions for IG (32.7 MW) assure the gasification temperature of 1200 °C in the reactor. The composition of the syngas produced after the pyrolysis/gasification step is reported in Table 2 for both configurations in the reference conditions. CO and H₂ are the most abundant products. Among the other component, CO₂ and residue H₂O are significant, CH₄ (not thermodynamically favored) and H₂S (from the sulfur content of the parent coal) are in traces. The effect of the operating conditions is evaluated comparing the results reported in Table 3. The gasification temperature, the concentration of hydrogen after the gasification and after the shift reaction, the flowrate of hydrogen produced are monitored in all cases. The first set of results are obtained varying the C/S ratio at fixed C/O ratio for the DG configuration. Variations from -17% to +25% are studied. The higher the C/S ratio, the higher the gasification temperature, the lower the flowrate of hydrogen produced. Consequently, the hydrogen production efficiency increases with the amount of steam fed to the gasification, because a high excess of steam favors the coal gasification conversion. The vaporization of an excess of water requires considerable energy, so the power efficiency of the process shows a maximum. In practice, a low gasification temperature is not suitable because would require a high residence time in the reactor. η_H and η_P in reference conditions are 57% and 0.8%, respectively. The latter value denotes the low net power produced in the process. Energy demand and heat consumption are actually very high (especially for the air separation unit, which requires approximately 18 MW in the reference conditions). As a matter of fact, the process configuration and specific assumptions (C/O imposed to furnish the strictly necessary heat) are studied to maximize the hydrogen production.

The second set of results in Table 3 are obtained varying the C/O ratio at fixed C/S ratio for the DG configuration. Decreasing C/O of 7% (thus increasing the flowrate of oxygen fed to the process), the gasification temperature increases enormously (1376 °C). The high amount of oxygen consumes the carbon of the coal, favoring the formation of CO₂ at the end of the process. In this case, η_H decreases from 57% to less than 54%. Vice versa, increasing C/O of 13%, the gasification temperature decreases dramatically (970 °C), producing significant amount of CH₄ and decreasing the final production of hydrogen (η_H is approximately 54%).

Table 1. Proximate and ultimate analysis and heating value of coal.

	Proximate analysis (%wt dry)			Ultimate analysis (%wt dry)					HV (MJ/kg)
	VM	FC	Ash	C	H	N	Cl	S	
HS coal	32.2	57.3	8.9	69.7	4.44	1.2	0.09	0.82	29.3

Table 2. Composition of syngas after the gasification (in reference conditions)

(mol fraction)	H ₂ O	O ₂	N ₂	CO	CO ₂	H ₂	CH ₄	H ₂ S
DG configuration	0.12	1.4 E-14	0.0006	0.494	0.078	0.303	0.0004	0.001
IG configuration	0.0156	6 E-17	0.0008	0.426	0.005	0.535	0.016	0.0012

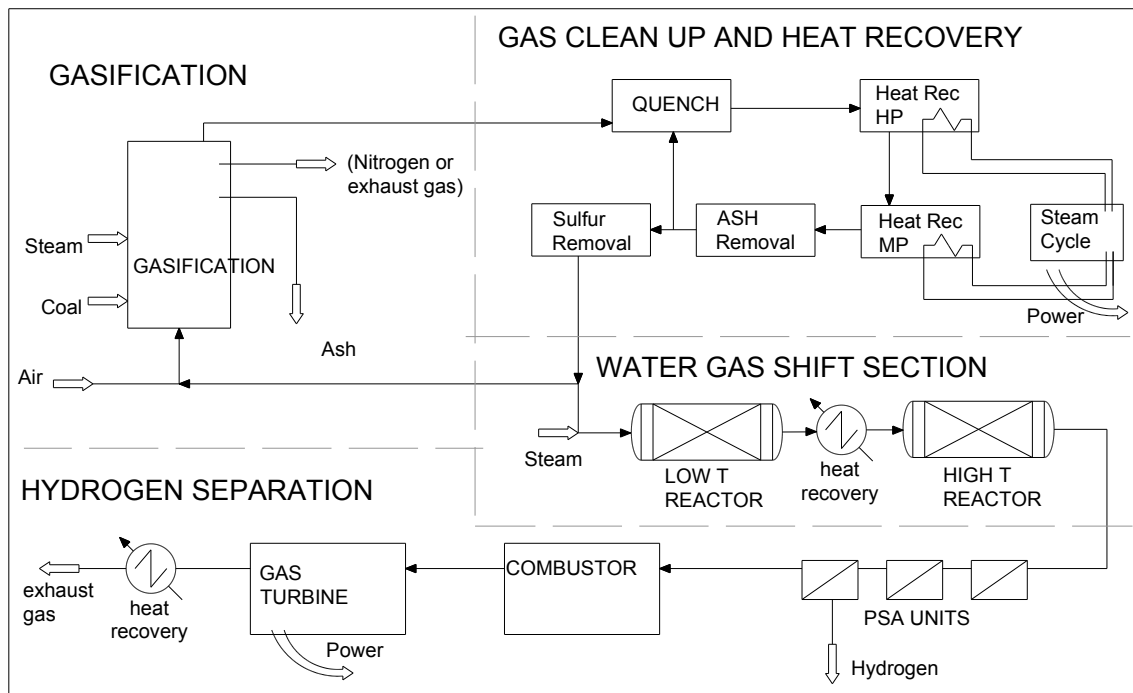


Fig. 2. Flowsheet of the coal gasification process for hydrogen production. The gasification options are depicted in Figure 1: nitrogen is produced in the direct gasification as by-product of the air Separation Unit.

The third set of results reported in Table 3 are obtained varying the C/S ratio and adjusting the heat furnished by the combustor to guarantee the temperature of 1200 °C in the IG configuration. As in the previous case, varying C/S from -18% to +24% respect to the reference case, η_H decreases because the high amount of H₂O in the gasifier favors the equilibrium of the reactions producing hydrogen. In these cases, a maximum in the net power efficiency is not observed. However, a high flowrate of steam requires a high energy to heat and vaporize the water, as in the previous case.

Table 3. Comparison of the sensitivity analysis results

Coal/Steam	Coal/O ₂	$y_{H_2, gasif}$	T_{gasif} (°C)	$y_{H_2, shift}$	F_{H_2} (kg/s)	H	P
Direct Gasification Configuration– effect of C/S ratio							
1.60	1.24	0.305	1172	0.51	0.76	58.17	0.25
1.92	1.24	0.309	1209	0.51	0.74	57.07	0.83
2.13	1.24	0.305	1230	0.50	0.71	54.62	0.75
2.40	1.24	0.303	1252	0.49	0.68	52.01	0.44
Direct Gasification Configuration – effect of C/O ratio							
1.92	1.40	0.315	970	0.50	0.71	54.27	1.07
1.92	1.24	0.309	1209	0.51	0.74	57.07	0.83
1.92	1.15	0.278	1376	0.50	0.70	53.66	0.62
Indirect Gasification Configuration							
1.58	-	0.535	1201	0.62	0.60	46.34	7.17
1.92	-	0.545	1209	0.62	0.56	42.65	6.19
2.38	-	0.558	1224	0.60	0.50	38.46	5.56

Values of C/S in the same range allow to compare the DG and IG configurations, as for H₂ and net power produced. The highest hydrogen production efficiency is achieved in the DG configuration η_H 57% (against 43% for the IG configuration in the same conditions), 0.74

kg/s of pure hydrogen are produced (against 0.56 kg/s). Vice versa, the net power efficiency is higher for the IG configuration (η_p is 6.2%) than for the DG configuration (η_p is 0.83%).

Considering the consumes and the performances of prototypes realized at present, the production of approximately 0.7 kg/s of pure hydrogen in a power plant can meet with the demand of 100'000 vehicles or, alternatively, 6700 buses [9]. Considering a penetration of 2% of hydrogen vehicles and 40% that of public buses, in a realistic short-term scenario, the process studied in this work meets with the demand of a 2'600'000 equivalent inhabitant area.

5. Conclusions

A process optimization method has been developed and applied to study the coal gasification for the production of hydrogen. The boundary definition and the identification of main units are basic steps for the process analysis. Thermodynamic databases, parametric models (for the pyrolysis and gasification steps) and a steady state simulation software are fundamental tools, which should be appropriately combined to gain the specific advantages. Operating and monitoring variables as well as defined performance targets should describe synthetically and precisely the entire process to allow the comparison of different cases and the evaluation of the effect of sensitivity parameters. The results of two configurations (direct and indirect gasification) have been discussed varying the coal to steam and coal to oxygen ratios, evaluating the hydrogen production and net power efficiencies. More details were given for the model of the pyrolysis/gasification unit. This is a starting work to verify the validity of the process optimization method. Further investigations will be carried out to assess the feasibility of advanced process options (e.g. CO₂ sequestration), the possibility of integrating the process with a centralized power plant and the suitability of environmental targets.

6. References

- [1] Dunn S. Hydrogen futures: toward a sustainable energy system. *Int. J. Hydrogen Energy* **27**, 235-264 (2002)
- [2] Stiegel G.J., Maxwell R.C. Gasification Technologies: the path to clean, affordable energy in the 21st century. *Fuel Processing Technology* **71**, 79-97 (2001)
- [3] Chiesa P., Consonni S., Kreutz T., Williams R. Co-production of hydrogen, electricity and CO₂ from coal with commercially ready technology. *Int. J. Hydrogen Energy* **30**, 747-767 (2005)
- [4] Donatini F., Gigliucci G., Morganti M, Biagini E., Tognotti L. Hydrogen Production by Pyrolysis/Gasification of Solid Fuels in Fluidized Bed Reactors. *Proc. of the 28th Meeting of the Italian Section of the Combustion Institute. Combustion and Urban Areas*. July 4-6, 2005 Naples (Italy)
- [5] Biagini E., Tognotti L., F. Donatini. Integrated Systems for Hydrogen Production and Use in Distributed Generation. *Proc. of the 2nd International Conference on Hydrogen Era. H2www@Sicily*. October 16-19, 2005 Palermo (Italy)
- [6] Spath P.L., Mann M.K. Biomass Power and Conventional Fossil Systems with and without CO₂ Sequestration – Comparing the Energy Balance, Greenhouse Gas Emissions and Economics. *Technical report – US Department of Energy Laboratory*, Contract No. DE-AC36-99-GO10337 (2004).
- [7] Fletcher T.H., Kerstein A.R., Pugmire R.J., Solum M., Grant D.M. A Chemical Percolation Model for Devolatilization. *Sandia Technical report SAND92-8207* (1992)
- [8] Ruettinger W., Ilinich O., Farrauto R.J. A new generation of water gas shift catalysts for fuel cell applications. *J. Power Sources* **118**, 61-65 (2003).
- [9] Gigliucci G., Schiavetti M. Analisi tecnico-economica della produzione di idrogeno per l'autotrazione nelle centrali Enel a carbone. *Technical report Enel*, Sept. 2003