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HYDROGEN PRODUCTION THROUGH CO-GASIFICATION OF COAL AND BIOMASS WITH CARBON DIOXIDE CAPTURE

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ABSTRACT. This paper presents technical aspects of hydrogen production technology through co-gasification of coal and biomass based on modeling and simulation of the process. Three plant configurations containing entrained-flow gasifiers were studied. A performance analysis regarding the energy efficiency of the process, carbon conversion rate and the carbon dioxide capture rate have been carried out. A significant advantage of gasification process described in this paper is the limitations of greenhouse gas emissions through acid gas removal **unit (carbon dioxide capture, hydrogen sulfide processing)**.

Keywords: *hydrogen production, gasification, entrained-flow reactors, energy efficiency, CO_2 capture and storage*

INTRODUCTION

Introducing hydrogen in the energy system as a complimentary energetic vector to electricity represents an issue of most importance in Europe due to the significant advantages it offers [1-3]. Among the advantages of using hydrogen in the energetic system as a complimentary energetic vector to electricity one can mention: low greenhouse gases emission, increased electricity delivery safety, increased economic performance [4]. Hydrogen can be obtained through a variety of technological, chemical, biochemical or electrochemical processes [5]. The choice of the most suitable options to produce hydrogen is influenced by a series of factors such as: raw materials resources, utilities, the possibility of delivering the product, etc.

Through gasification, the energy of solid or liquid fuel (fossil fuel or biomass or industrial or housework waste) is turned into a synthesis fuelling gas (a mixture containing mainly CO and H_2) which can be processed to generate hydrogen as well as a large variety of chemical compounds (methanol, ammonia, urea, synthetic fuels, etc.) [6]. The raw material used in the process of gasification described in this paper is a mixture of 80% coal and 20% biomass – in this

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case sawdust. The situation of solid fossil fuel is much better than that of oil and natural gas because they are uniformly spread all over the Earth and due to the sustainable deposits covering a longer period of time in comparison with the annual level of energy consumption, thus resulting better continuity for ensuring raw materials supply [7]. One should stress the fact that this technology is viable only if the carbon dioxide emissions, are captured and stored.

The hydrogen production plant based on gasification of coal and sawdust with carbon dioxide capture and storage has the following sub-systems: (I) Gasification of a mixture of coal and biomass, (II) Catalytic conversion of carbon monoxide ("Water Gas Shift – WGS"), (III) Acid gas removal unit ("Acid Gas Removal - AGR"), (IV) Hydrogen purification („Pressure Swing Adsorption – PSA").

Coal and biomass gasification. Currently the majority of gasification processes are based on entrained-flow reactors that operate with feed and blast in co-current flow (oxygen is used as oxidation agent and steam as moderator). The feed is ground to a size of 100 μm or less (that allows transport in the gas and high mass transfer coefficient). The residence time in these gasifiers is in the range of seconds. As a result high operating temperatures are required for a good conversion rate [8]. The outlet gas temperature is between 1250-1600°C, above the ash melting point, which makes all entrained-flow gasifiers operate in the slagging range [9, 10]. High temperatures also lead to high oxygen consumption. Main advantages presented by this type of gasification reactors are: the ability to handle practically any coal as feedstock, to produce a clean and tar-free gas, the ash is produced in the form of an inert slag, a high carbon conversion of over 99%, high quality synthesis gas because of the low methane content [8]. Three plants configuration based on entrained flow reactors were analyzed in this paper.

Tabel 1. Gasifiers parameters [8]

Technology	Stage	Feed	Flow	Reactor wall	Syngas cooling	Oxidant
Siemens	1	dry	up	Membrane	Water	Oxygen
Shell	1	dry	up	Membrane	Gas	Oxygen
Texaco	1	slurry	down	Refractory	Water	Oxygen

Catalytic conversion of carbon monoxide. The catalytic conversion of carbon monoxide with water vapor ("water-gas shift - WGS") takes place in an installation with two reactors, with intermediary cooling between them, operated in an adiabatic mode. A sulphur tolerant catalyst is used, based on cobalt and molybdenum [5, 11]. The reaction of catalytic conversion of carbon monoxide with water vapor follows the next equation:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$

This is an exothermal reaction also called „shift” or „water gas shift - WGS”. It is used in the hydrogen production plant with carbon dioxide capture and storage in order to focus the syngas thermal energy (mixture of hydrogen and carbon monoxide) as hydrogen and to focus the chemical species which contain carbon as carbon dioxide [7].

Acid gas removal unit. Separation of acid gases (carbon dioxide and hydrogen sulfide) is achieved through the process of gas liquid absorption by using Selexol$^{\circledR}$ as a solvent. This is a physical solvent, a mixture of dimethyl ethers of poly- ethylene glycol whose chemical formula is: $CH_3(CH_2CH_2O)_nCH_3$ where “n” varies between 3 and 9.

Hydrogen Purification („Pressure Swing Adsorption – PSA”). Hydrogen purification is made through pressure modifications (reduction) – this technique is called „Pressure Swing Adsorption – ” [12,13]. High pressure is needed to ensure long distance transport from production sites to end-users with low energy consumption (pressure drop along pipes network). High purity hydrogen is essential to its use in transport sector (99.99% purity is required for compatibility with PEM fuel cell) [5].

RESULTS AND DISCUSSION

The modeling and simulation of hydrogen production process through co-gasification of coal and biomass, was made using chemical process simulation software (ChemCAD) [14]. The thermodynamic package used in the simulations is based on a modified SRK model.

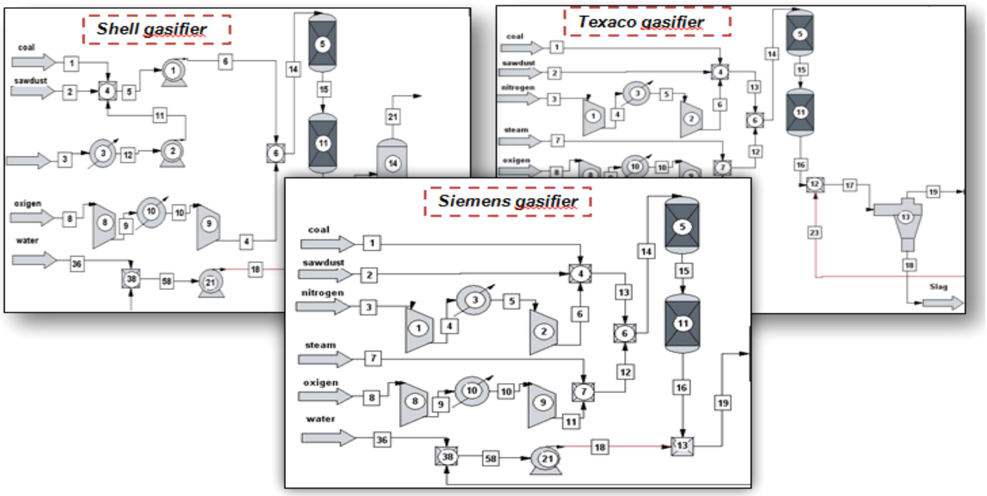


Figure 1. Gasification, WGS, PSA units

Three case studies were analyzed: (I) dry feed gasifier with nitrogen as transport gas and water quench for cooling the gas (Siemens); (II) dry feed gasifier with nitrogen as transport gas and gas quench for cooling the resulting syngas (Shell); (III) high pressure slurry feed gasifier with water quench (Texaco).

The main model assumptions used for the modeling and simulation of the gasification process are presented in the Table 3. The necessary data are derived from the literature [15-17].

Table 2. Model assumption

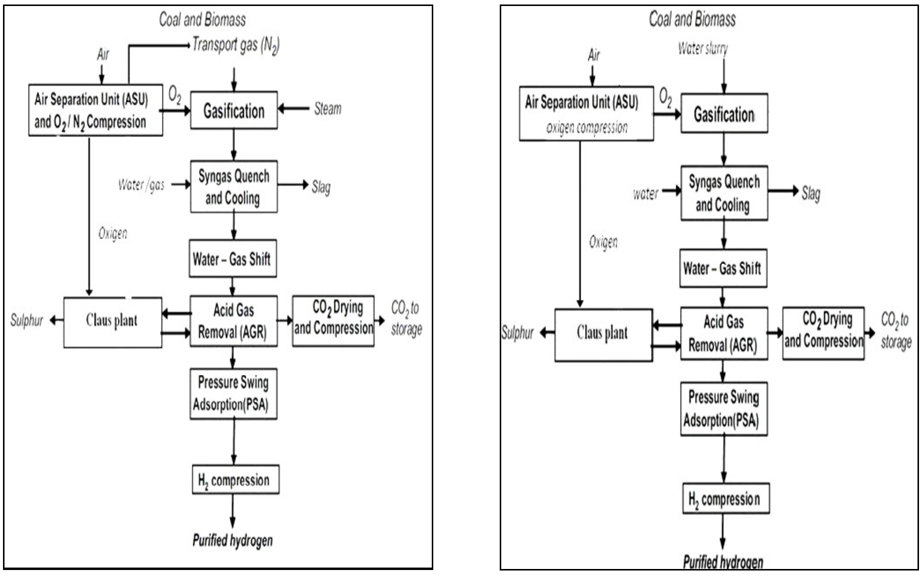
Gasification unit	P: 40 bar (dry feed)/ 70 bar (slurry feed); T: 1400°C (dry feed)/ 1300°C (slurry feed); Carbon conversion rate: 99.99%; Coal concentration in the water slurry: 62 wt%;
Water gas shift unit	Catalyst type: sour shift catalyst, temperature range: 250–500°C; Carbon monoxide conversion rate: 96-98%; Two adiabatic catalytic beds;
Acid gas removal unit	Solvent: Selexol®; Two stages: first H_2S removal, second CO_2 removal; First stage: Selexol® flow preloaded with CO_2; Solvent refrigeration level: +5°C; Oxygen-blown Claus plant (95% vol.); H_2S-rich gas composition to Claus plant: >21% H_2S (vol.); Tail gas is recycled to H_2S absorption stage; Second stage: CO_2 removal: absorption tower–flash; Delivery temperature and pressure: 35°C, 110 bar; Carbon dioxide capture rate: 92%-96%;
Hydrogen purification unit	Hydrogen purity: 99.99% (vol.); Hydrogen purification yield: 85%;

Feedstock for the gasification reactors consists of coal and biomass (blend mass ratio 80% coal, 20% biomass). Raw material is fed in the gasifiers using nitrogen as transporting gas (dry feed) and water suspension (slurry feed). Oxygen is used as an oxidant agent. The resulting syngas main components are: hydrogen, carbon monoxide, carbon dioxide, nitrogen, water. The highest hydrogen and carbon monoxide content is obtained in the case of the Shell reactor. The slurry feed reactor (Texaco) has the highest carbon dioxide content and the lowest carbon monoxide content (because part of the carbon from the coal must be oxidized totally to carbon dioxide to provide the heat necessary to vaporize the water from the slurry [18]). Carbon conversion rate is 99.99% in all three cases.

The resulting syngas goes to the water gas shift unit. The catalyst used is cobalt–molybdenum based, with an operating temperature range between 250–500°C. Water/carbon monoxide ratio is between 2.08 and 3.1 and the carbon monoxide conversion rate is of 96-98%. The heat that results from the process of carbon monoxide catalytic conversion is used to generate medium and low pressure steam (the steam covers part of the heat requirements of the plant).

After the water gas shift conversion, liquid water is separated, and then the resulting syngas goes to the acid gas removal unit. The AGR unit structure consists in two stages. First, hydrogen sulfide is almost 100% removed with a flow of Selexol® preloaded with carbon dioxide, then H_2S is partially oxidized to sulfur in the Claus plant. In the second stage of the AGR unit carbon dioxide is separated (configuration: absorption tower–flash). The Selexol® solvent is regenerated using a system of four flashing vessels (pressure in the flash vessels: 8, 5, 2, 1 bar). The CO_2 is compressed in five stages with inter cooling and sent to storage. The carbon dioxide capture rate is between 92-93% in dry feed configuration, and 96% in slurry feed (because of the high operating pressure). Overall CO_2 removal yield is about 96-97%.

The flow free of acid gas is sent to the purification unit (hydrogen purification yield: 85%). The hydrogen flow obtained has 99.99% (vol.) purity and pressure of 27 bar (dry feed)/ 53 bar (slurry feed). Next is compressed at 70 bar to ensure pipeline transportation. The figure below present the scheme of hydrogen production through gasification:



Dry feed ***Slurry feed***

Figure 2. Scheme of hydrogen production through gasification

To obtain a better view regarding hydrogen production plant efficiency, with carbon dioxide capture and storage, the performance indicators presented below were calculated. Energy efficiency of the plant (EEP%) was calculated using the formula [7]:

$$\mathrm{EEP}\ (\%) = \frac{(\text{Hydrogen thermal energy} + \text{ electrical power generated})}{\text{Raw material thermal energy}} \quad (2)$$

The thermal energy of hydrogen and raw material was calculated as the product between flows in kg/h and lower heating value in MJ/kg. In all the three cases analyzed, 658.2 MW fuel input was considered. The table below presents the energy balance of all plant configurations assessed in this paper:

Table 3. Plants energy eficency

Case study		**Siemens**	**Shell**	**Texaco**
Parameter	**Units**	**Value**	**Value**	**Value**
Coal flow	kg/h	73520	73520	73520
Sawdust flow	kg/h	18000	18000	18000
Coal heating value	MW	567.7	567.7	567.7
Sawdust heating value	MW	90.5	90.5	90.5
Fuel input	MW conssumed	658.2	658.2	658.2
H_2 power	MW generated	400	390	360
Gas thermal energy	MW generated	78	73	95
Generated power from PSA tail gas	MW generated	43	41	52.3
Ancillary power consumption	MW consumed	43.7	38.88	61.35
Generated power (steam turbine)	MW generated	27.2	37.97	43.08
Net power output	MW	26.4	40.11	34.03
Plant efficency	**%**	**64.8**	**65.4**	**60**

The slurry feed based plant configuration has a lower efficiency than the dry feed ones, of about 5% points, mainly due to the heat requirement for vaporizing the water in the slurry. But this configuration has the advantage of producing high pressure hydrogen that can be easily transported through pipelines without any additional power consumption for compression.

To evaluate the environmental impact determined by the hydrogen production plant the carbon dioxide capture rate was calculated (%of carbon content of the input fuel that was captured). As can be seen in Table 4, all plant configurations analyzed in this paper have a carbon dioxide capture rate of over 90%. The dry feed gasifier cases present a lower carbon dioxide capture rate (92%, 93%) than the slurry feed gasifier case (96%) due to the lower pressure of the AGR system (27.8 bar compared to 52.8 bar).

Table 4. Carbon dioxide capture rate

Case study	**Siemens**	**Shell**	**Texaco**
Flowsheet	CO_2 flowsheet (kmol/h)	CO_2 flowsheet (kmol/h)	CO_2 flowsheet (kmol/h)
Storage			
CO_2	4698.368	4739	4928
CO	10.0755	9.1	7.44
CH_4	0.617	0.46	2.2
Total storage	4709	4749	4938
Emissions			
CO_2	278.58	251	127
CO	122	141	77.8
CH_4	0.03	0.32	0.06
Total emisisions	401	393	205
Net carbon flow	5110	5142	5143
CO_2 capture rate	**92%**	**93%**	**96%**

CONCLUSIONS

This paper presents technical aspects of ~400 MW hydrogen (99.99% vol. purity) production technology through co-gasification of coal and biomass (blend mass ratio 80% coal, 20% biomass) with carbon dioxide capture and storage. The plant configurations assessed are based on three types of entrained-flow gasifiers (Siemens, Shell, Texaco). A performance analysis regarding the energy efficiency of the process, carbon conversion rate, syngas composition and the carbon dioxide capture rate was carried out. Based on the simulation results, the following conclusions are drawn: i) the slurry feed based plant configuration has a lower energy efficiency than the dry feed one, ii) carbon conversion rate is 99.99% in all the three cases, iii) an important advantage of the gasification process described in this paper is the limitation of greenhouse gas emissions through carbon dioxide capture (carbon dioxide capture rate is over 90%).

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