Carbon dioxide emission in hydrogen production technology from coke oven gas with life cycle approach

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Abstract. The analysis of Carbon Footprint (CF) for technology of hydrogen production from cleaned coke oven gas was performed. On the basis of real data and simulation calculations of the production process of hydrogen from coke gas, emission indicators of carbon dioxide (CF) were calculated. These indicators are associated with net production of electricity and thermal energy and direct emission of carbon dioxide throughout a whole product life cycle. Product life cycle includes: coal extraction and its transportation to a coking plant, the process of coking coal, purification and reforming of coke oven gas, carbon capture and storage. The values were related to 1 Mg of coking blend and to 1 Mg of the hydrogen produced. The calculation is based on the configuration of hydrogen production from coke oven gas for coking technology available on a commercial scale that uses a technology of coke dry quenching (CDQ). The calculations were made using ChemCAD v.6.0.2 simulator for a steady state of technological process. The analysis of carbon footprint was conducted in accordance with the Life Cycle Assessment (LCA).

1 Introduction

Coal is one of the most important primary energy sources and, in contrast to oil and natural gas, its resources are much larger and located in all geographical regions [1-2]. World coal resources, estimated by EURACOAL [3] account 726 mld tones, while according to WEC - 826 mld tones [4]. Coal is not only used as a fuel to generate heat and electricity, but also as a raw material in pyrolysis process, gasification and for direct hydrogenation of coal.

Nowadays, excluding electric power industry, the pyrolysis process is the most popular way of coal processing. The raw material is heated without the access of oxygen to about 1300 K and the main products are: coke, coke oven gas, tar, benzol and depending on the gas purification technology: ammonium sulfate, sulfur or sulfuric acid. Currently, about 80% of the global coke production is located in Asia, including nearly 70% in China. CRUs forecasts [5] confirm, that a similar proportions in the sector will sustain in the coming years. According to CRU - world coke production will rise and the estimated production in 2017 will reach about 793 million tones [5, 6-8]. Coking plants creates a threat to the environment [9-11]. It is worth noting that coking process gives the possibility of obtaining hydrogen from purified coke oven gas - which contains more than 50 vol.% H_2 [12, 13].

Hydrogen is not present in large quantities and concentrations on Earth [14]. It is mainly obtained from biomass, water and fossil fuels due of their wide availability [15]. Interest in hydrogen as a fuel [16, 17] due to the fact that during reaction with oxygen a significant amount of energy is being released - 143.1 MJ/kg and the only reaction product is water. Hydrogen being used in fuel cells allows direct conversion of chemical energy in the reaction with oxygen into electricity. It is also a base material of many chemical syntheses, in which many substances, both organic and inorganic may be produced [18]. Global hydrogen production comes mainly from fossil fuels processing without CCS (*Carbon Capture and Storage*) technologies: 48% from natural gas, 30% from the refinery off-gases, 18% from coal and the rest comes from electrolisys and biomass [19-24].

Environmental footprints are widely use to assess the impact of technology on the environment. Scientists have developed and implemented a lot of indicators showing the impact of human activities on the environment, for example: energy footprint [25], water footprint [26], nitrogen footprint [27] and carbon footprint [28]. Carbon footprint (CF) is the most objective method of assessing the technology impact on the environment in the aspect of the greenhouse effect [29, 30]. CF is a measure of the total amount of Greenhouse Gas emission (GHG - greenhouse gas), both direct and indirect, throughout the life cycle of a product or technology. The methodology of analysis and calculation of the CF is based on Life Cycle Assessment (LCA), a research into potential aspects of environmental impact in the whole life cycle that is, on each of its stages – from obtaining raw materials,

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through production, until the utilization and/or recycling of the main product [31-36].

The aim of this study was to analyze the CF of hydrogen production from purified coke oven gas. Calculations were made and an evaluation of indicators of direct and indirect CO_2 emissions resulting from the cycle of obtaining hydrogen were performed, including the following steps: coal mining, transport of coal to coking plants, coking process and hydrogen production from purified gas, and operations of CO_2 capture and sequestration. For this calculations methodology of LCA described in ISO 14040:2009 was used [37].

2 General information, data and assumptions

An analysis of CF for the technology of hydrogen production from coke oven gas derived from coking of coal blend with the characteristics given in Table 1 was performed. CF of the hydrogen production was calculated in accordance with standard ISO 14067:2014 [38] and included both direct and indirect emissions associated with electricity and heat consumption during coal mining, coal transport from mine to coking plant, coal blend preparation, coking process, cooling and cleaning gas and its reforming.

Table 1. Characteristics of coal blend

Mark	As received	Dry basis
C [%]	77.4	84.3
H [%]	4.2	4.6
N [%]	1.2	1.3
S_t [%]	0.5	0.5
O [%]	2.4	2.6
W_t [%]	8.2	-
A [%]	6.1	6.6

2.1 Coal mining processes

Investigated coking coal blend (Tab. 1) is composed of several coking coals obtained from mines with high absolute methane content. Therefore, the assumption was made, that 60% of methane is captured and used to produce electricity and heat, while the rest present in the ventilation air (methane concentration below 2%) is catalytically combusted. To estimate the values of CO_2 emission in the production of coal was assumed that: to produce 1 Mg of coal a mine consumes on average 68.02 kWh of electric energy and 43.98 MJ of heat (by commercially available technology),
- the results of calculations show that in the case of the ventilation air containing 0,5% of methane, it is necessary to provide the 486 kJ heat on 1 m^3 CH_4 for the catalyticall combustion process
- emission of CO_2 from burning methane at the power plant is 1.9643 kg CO_2/m^3 and 1.9951 kg CO_2/m^3 from catalytic combustion,

- the rate of electricity consumption to produce compressed air is 0.0833 kWh/m^3,
- in Polish conditions production of 1 kWh of electricity generates CO_2 emission equal to 0.9124 kg, while producing 1 GJ of heat energy generates 63.4600 kg CO_2 emission.

Based on the above the calculated CF from the combustion of methane is 20.6027 kg CO_2 per 1 Mg of mined coal, while the catalytic combustions generates CF value of 33.2449 kg CO_2/Mg_{coal}. As a result of methane combustion 28.4317 kWh of electricity, 0.0701 GJ of heat and 5.1 m^3 of compressed air per 1 Mg of coal is obtained. This allows to save 0.4248 kWh/Mg. Thus, coal mining under the precise conditions present in the mine consumes net 39.1590 kWh / Mg_{coal} electricity and -0.0261 GJ /Mg heat. A negative value means, that the amount of heat produced by the power plant (at the mine) is greater than mine requires.

2.2 Coal transporting to coking plant

Based on the data obtained from the company transporting coal from the mine to the coking plant a rate of electricity consumption during by rail transportation (0.0789 kWh/Mg·km) was assumed. This generates indirect emission of carbon dioxide associated with the transport of raw materials 0.072 kg CO_2/Mg·km (0.003 kg CO_2/(GJ·km)). It was assumed that coking plant is located 100 km from the mine.

2.3 Coking process

The coking process is carried out in the chambers of the coke oven battery system with a volume of 30 m^3 useful chamber. The battery is heated exclusively by own coke gas. After completion of the coking process, the basic product - coke at a temperature of 1000°C, is pushed out of the chamber, cooled, sorted and transported to customers. Raw coke oven gas is purified by ammonia absorption in the scrubber, where the reduction of H_2S and NH_3 to a level below 0.5 g/m^3 and 0.03 g/m^3 is obtained, respectively. The composition of raw coke oven gas is given in Table 2. The mixture of steam and gas from absorption system is moved to catalytic decomposition of NH_3 and sulfur production by Claus process. In the next step, benzol is absorbed from purified gas by ammonia method. The purified gas is divided into two equal streams, one of them is used for own coking plant requirements and the other is used for the hydrogen production.

Energy supply for preparation and coking coal departments were estimated based on the information on technological solutions in coking plants available on a commercial scale, specifically these using technology of coke dry quenching. During coke dry quenching a large part of the physical enthalpy of the hot coke is recovered and it is used to produce steam and electricity for coking plants own consumption. Summary consumption of energy factors for preparing and coking processes and coal derivatives department for 1 Mg of dry coal are given in Table 3.

Table 2. Composition of raw coke oven gas

Component	m/m%	v/v%
H_2	6.0	41.7
CO	4.6	2.3
CH_4	22.6	19.7
CO_2	3.1	1.0
C_2H_6	5.6	2.6
H_2S	1.4	0.6
NH_3	2.3	1.9
H_2O	36.2	28.0
Benzol	4.3	0.8
Tar	14.0	1.5

Table 3. Usage of energy and coke oven gas for coking plant

Energy carrier	Expenditure	Income	Difference
Electricity [kWh/Mg_{ws}]	74.07	39.63	-34.44
Heat [GJ/Mg_{ws}]	1.57	1.32	-0.25
Coke oven gas [MJ/Mg_{ws}]	2687	6560	+3873

2.4 Hydrogen production

After benzol absorption step, gas stream is being subjected to the reforming technology, which comprises the following process units: coke oven gas reforming system, oxygen production installation, CO conversion system and the hydrolysis of COS, desulphurization system and CO_2 removal system, H_2 separation system and other plant. The calculations for hydrogen production were made using ChemCAD v.6.0.2 simulator for a technological process in a steady state. Calculations were made for the following assumptions:

• cleaned coke oven gas was used in reforming system at 25°C and saturated with water vapor and tar,

• battery heating uses 50% of the coke oven gas mixed with purified residual gas,

• separated in the Selexol system compounds of sulfur are moved to Claus installation, belonging to the technological system of coking plant

Table 4 shows the mass balance for hydrogen production process from purified coke oven gas. Table 5 shows the consumption of electricity according to installation requirements. Table 6 presents efficiency of obtaining hydrogen from purified coke oven gas, which was calculated as the ratio of chemical enthalpy of products and the enthalpy of chemical raw materials, i.e. excess gas and tar.

The separation of CO_2 generated during the hydrogen production from purified coke oven gas was included. As a result carbon dioxide is being produced as a byproduct, in an amount of 3 835 Mg/h (28 555 Mg/year), with a degree of purity of over 99%. It can be a commercial product or a storage object. In the case of sequestration of carbon dioxide separated during hydrogen production from coke oven gas, compression, transportation and congestion in selected places of geological storage are required.

Table 4. Mass balance for hydrogen production plant

Stream name	[Mg/24 h]	[Mg/year]	Purified coke oven gas [kg/kg gas]	Gas for reformer[kg/kg gas]	[kg/kg H_2]
Expenditure/production					
In (entrence)					
1. Coke oven gas	47	14 706	1.00	1.04	4.30
2. Oxygen	36	11 099	0.75	0.79	3.24
3. Tar	15	4 579	0.31	0.32	1.34
4. Water supplement	44	13 775	0.94	0.97	4.03
5. Steam	40	12 360	0.84	0,87	3.61
Summary	**182**	**56 520**	**3,84**	**4,00**	**16,52**
Out (exit)					
1. Hydrogen	11	3 425	0.23	0.24	1.00
2. CO_2	92	28 555	1.94	2.02	8.34
3. Acid gas	2	663	0.05	0.05	0.19
4. Gas for battery	31	9 553	0.65	0.68	2.79
5. Waste	45	13 939	0.95	0.99	4.07
6. Steam production	1	387	0.03	0.03	0.11
Summary	**182**	**56 523**	**3.84**	**4.00**	**16.52**

Assumptions concerning the conditions for the transport of carbon dioxide and its injection in geological deposits are:

• carbon dioxide will be transported in the liquid phase,

• the pressure at the inlet to a transport system (pipe) is 120 bar, which allows to transport of CO_2 at about 100 - 150 km distance and the congestion it in geological structures without additional compression.

The values of electric energy requirements for CO_2 compression system for transport and storage, and corresponding carbon dioxide emissions are shown in Table 7. Table 8 shows the CF associated with net production of electricity and heat for hydrogen production from purified coke oven gas.

Based on the collected data (Tables 3-5) from process simulator (ChemCAD) production indicators and consumption of electricity and heat throughout the life cycle of the technology of hydrogen production from purified coke oven gas at all process stages were calculated. The values of these indicators are referenced to the unit mass of coking coal and the unit mass of produced hydrogen.

Table 5. Electric energy usage for hydrogen production plant

Department	Installed power [kWe]	Expediture of energy		
		kWe/kg gas	kWe/kg H_2	GWh
1. Oxygen	564	0.29	1.23	4.20
2. Gas reformer (power pumps)	17	0.01	0.04	0.10
3. Gas pressing	147	0.08	0.32	1.10
4. Desulphurization	-	-	-	-
5. Gas cooling system	12	0.01	0.03	0.1
6. Gas compresion	1 177	0.62	2.56	8.80
7. Removal of acid gas - Selexol	213	0.11	0.46	1.60
8. Claus/Scot-installation	-	-	-	-
Summary	**2 130**	**1.12**	**4.64**	**15.9**

Table 6. Process efficiency

Process efficiency	Wd
Gas after reformer	90.24 %
Gas PSA	85.02 %
Hydrogen	71.28%

Table 7. Electric energy requirement for the CO_2 compression step and related emissions.

Parameter	Value
CO_2 stream for sequestration, Mg per year	28 559
CO_2 stream for sequestration, kg CO_2/Mg$_{coal}$	227.24
CO_2 stream for sequestration, kg CO_2/Mg H_2	8 346.03
Compression electricity power, MWe	0.32
Energy consumption for compressing, kWh/Mg$_{coal}$	19.13
Energy consumption for compressing, kWh/Mg H_2	702.71
CO_2 emission indicator, kg CO_2/Mg$_{coal}$	**17.46**
CO_2 emission indicator, kg CO_2/Mg H_2	**641.16**

Based on the above-mentioned indicators, CF associated with the consumption of heat and electricity in the coking process and coke oven gas reforming in the hydrogen production were calculated. Coke oven gas is only one of the products of the coking process therefore, to the individual coking products used to produce hydrogen, carbon dioxide emissions in proportion to their contribution to the total amount of energy in all products of coking has been attributed.

Based on the above-mentioned information about distribution of energy in the coking products and basic balance data of the major process streams (ChemCAD), share of CO_2 emission from the coking process connected to raw materials supplied to reformer have a value of 0.1465 for hydrogen production from purified coke oven gas.

Table 8. CF related to the production of net electricity and heat for the hydrogen production from purified coke oven gas.

H_2 production	CO_2 emission indicators related with net production of electricity	
	Electricity	
	kg CO_2/Mg $_{coal}$	kg CO_2/Mg $_{H2}$
From purified coke oven gas.	119.36	4 383.84
Including: Coking process, H_2 production	4.23 115.13	155.19 4 228.66
	Heat	
	kg CO_2/Mg $_{coal}$	kg CO_2/Mg H_2
From purified coke oven gas	14.00	513.79
Including: Coking process, H_2 production	4.10 9.91	149.72 364.10
	Summary	
	kg CO_2/Mg $_{coal}$	kg CO_2/Mg H_2
From purified coke oven gas.	133.35	4 897.63
Including: Coking process, H_2 production	8.30 125.04	304.91 4 592.72

3 Conclusions

Hydrogen production technology from purified coke oven gas was subjected by CF analysis.

According to the LCA methodology including: coal mining, transport of coal to coking plants by railway, coking process with auxiliary operations, obtaining hydrogen from purified coke oven gas and sequestration of captured CO_2.

Hydrogen yield for considered technology was: 0.1859 Mg H_2 per 1 Mg of coal and 0.0076 Mg H_2 per 1 GJ net calorific value contained in coal. Conversion efficiency of chemical enthalpy is equal to 71.3%.

Carbon Footprint counted for 1 Mg of dry coal was 1 106.3 kg CO_2 and consists of emissions from the production of raw materials (14.0 kg CO_2/Mg$_{coal}$), transport of coal (1.1 kgCO_2/ Mg$_{coal}$), net energy consumption (938.9 kg CO_2/ Mg$_{coal}$), CO_2 indirect emission (22.5 kg CO_2/Mg$_{coal}$), CO_2 captured for sequestration (1689.8 kg CO_2/Mg$_{coal}$) and energy consumption for sequestration (129.8 kg CO_2/ Mg$_{coal}$).

CF counted in reference to 1 GJ of chemical entalphy contained in raw coal is 41.6 kg CO_2/ GJ, it consists of emissions from the production of raw materials (0,5 kg CO_2/ GJ), coal transportation (0.0 kg CO_2/ GJ), net energy consumption (35.3 kg CO_2/ GJ), CO_2 indirect emission (0.8 kg CO_2/ GJ), CO_2 captured for sequestration (63.5 kg CO_2/ GJ) and energy consumption for sequestration (4.9 kg CO_2/ GJ).

Value of CF in reference to 1 Mg of produced hydrogen was 5 463.7 kg CO_2. This contributes to the emissions resulting from the production of raw materials (69.3 kg CO_2/ Mg H_2), coal transportation (5.7 kg CO_2/ Mg H_2), net energy consumption (4637.4 kg CO_2/ Mg H_2), CO_2 indirect emission (110.2 kg CO_2/ Mg H_2), CO_2 captured for sequestration (8 346.0 kg CO_2/ Mg H_2) and energy consumption for sequestration (641.2 kg CO_2/ Mg H_2).

Acknowledgments

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