REDUCTION OF MERCURY EMISSIONS TO THE ATMOSPHERE FROM COAL COMBUSTION PROCESSES USING LOW-TEMPERATURE PYROLYSIS – A CONCEPT OF PROCESS IMPLEMENTATION ON A COMMERCIAL SCALE

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Key words: Mercury, coal, pyrolysis, emission control

Summary. This publication presents selected results of laboratory research on mercury removal from coal by the pre-combustion thermal treatment of fuel and a concept study of the process on a commercial scale. The concept assumes that a commercial-scale plant consists of drying and pyrolysis zones and that heat for the process is transported by flue gases from additional coal combustion. For the proposed plant configuration, a mass and energy balance was made. The thermal efficiency of the process amounts to 80 and 94% for brown and hard coal, respectively. Considering the significantly lower gas stream containing mercury and a higher mercury concentration than in the flue gases, the process could be more economically attractive compared to post-combustion technologies.

1. INTRODUCTION

Mercury (Hg) is a highly toxic element that poses a serious threat to human health. The data on mercury emission show that Poland is one of the leading European countries releasing mercury to the air [9]. The national emission of mercury to the atmosphere is estimated to be 15.9 Mg per year (2007) [7], and the main source of this emission is the combustion of fuels for energy production (64% share in the national emission load). The dominating role is played here by the power industry, which fires the largest amount of coal [7].

Current directions in the development of technology for the mercury emissions reduction from coal combustion processes can be divided into two basic groups:

– modifications of existing flue gas cleaning systems (reduction of flue gas temperature, sorbent injection, design modification),
– new technologies, including pre-combustion removal of mercury from coal and technologies for multipollutant emission control.

The method of Hg separation from fuel through thermal treatment (‘low-temperature pyrolysis’), before combustion is an interesting alternative to methods focusing on mercury removal from flue gases.

Because of higher mercury concentrations and substantially lower amounts of cleaned gas than in flue gas cleaning, mercury control technology by pre-combustion thermal treatment of coal may turn out to be cost competitive with traditional methods for mercury removal [11]. The possibility of using this process for the simultaneous desulphurisation and denitrification of fuel is an additional advantage [8, 12].

The most advanced work in the field of mercury removal from coal prior to combustion using thermal methods directed at practical process applications is carried out in the United States by the Western Research Institute (WRI) [4, 5, 6].

The research carried out at the Institute for Chemical Processing of Coal (ICPC, Poland) [1] has shown promise for the substantial reduction of mercury in fuel using the process of low-temperature pyrolysis. The process allows for high efficiencies in Hg separation without exerting a significant influence on the properties of cleaned coal (slight decrease in volatiles content and in chemical enthalpy of the fuel and an increase in calorific value).

2. SELECTION OF PROCESS PARAMETERS

The main parameters of the process have been determined through laboratory tests carried out for hard and brown coal. A detailed description of the test equipment, methodology and results of experiments is provided in [1] and [3].

Mercury removal from coal by thermal treatment is mainly affected by two parameters: process temperature and the fuel residence time in the reaction space. The efficiency of Hg removal, the properties of the fuel cleaned and the degree of chemical enthalpy reduction in the fuel stream fed to the system were assumed as basic criteria for the selection of the aforementioned parameters.

The research carried out on hard and brown coal in the temperature range of 220-250°C has shown that the optimum temperature for mercury separation is approximately 300°C. At this temperature, the process provides high Hg separation efficiencies (up to 65% for hard coal and 94% for brown coal) and does not deteriorate the cleaned fuel quality (improves certain parameters: reduces the moisture and sulphur content and increases the calorific value) or cause significant losses in the chemical enthalpy of the cleaned coal stream [1]. Figure 1 presents the effect of temperature on the efficiency of the mercury removal process and on chemical enthalpy changes in the fuel.

The results show that in the case of brown coal, the removal of Hg with high efficiency could proceed at lower temperatures. The selection of the optimal temperature should be the subject of detailed optimisation work performed for a specific fuel and for a selected technology of the process.

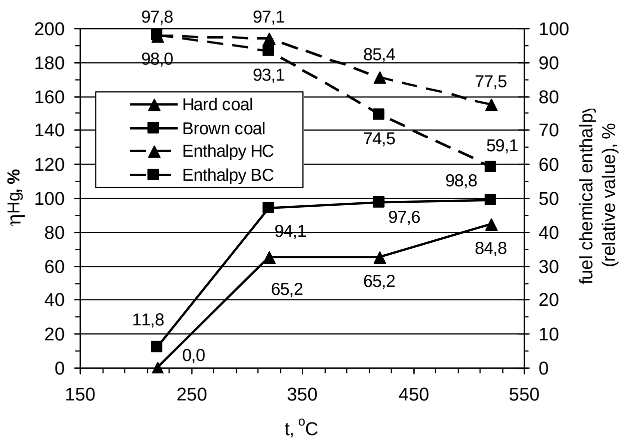

Fig. 1. Efficiency of Hg removal from hard (HC) and brown (BC) coal and relative value (to the raw coal) of chemical enthalpy of the fuel versus the process temperature

For a selected process temperature (300 °C), high efficiencies of mercury removal were obtained at relatively short residence times of 10-20 min. The increase in the residence time from 10 to 40 min resulted in an increase in Hg separation efficiency by about 9 and 3 percentage points for hard and brown coals, respectively. At the same time, the weight loss of the analysed specimens increased, which is related to the process of drying and pyrolysis. For the hard coal, the total weight loss was small, and taking the 2% water content of the sample into account, the weight loss related to pyrolysis amounted to around 3%. Much higher fuel degradation occurred in the case of brown coal. Weight losses at residence times of around 10 min were significant and amounted to approximately 10% (apart from the moisture removed) [3].

3. TECHNOLOGICAL CONFIGURATION

The following basic assumptions were made to analyse and develop the technological configuration of the system for mercury removal from fuel:

- The required temperature and the fuel residence time in the reaction zone were 300°C and 10-20 min, respectively.
- The system consisted of two basic parts: the drying and pyrolysis units.
- The flue gas (firing of additional amount of coal) was a heat carrier.

Figure 2 presents a technological diagram of the suggested system for mercury removal from fuel before combustion.

Coal fed into the system is divided into two streams. One stream is directed to a mill (2) and then to a combustion chamber (7) where the flue gas is generated, as it is the heat carrier in the process. In the case of pulverised fuel boilers, the combustion chamber (7) may be fed directly from a system of fuel milling and transportation to the boiler. The second stream of fuel (mercury removal) is directed to a fluidised bed dryer (10). After passing through the dedusting system (bag filter (12) for separation of fine fuel particles carried from the drying unit), the flue gas from the drying system is partly recirculated to the dryer and partly released to the atmosphere through a heat exchanger (22), where the water removed from the fuel is condensed and the heat recovered.

The dried fuel is directed to a pyrolysis reactor (in-direct heated rotary reactor) (19). From the pyrolysis reactor, mercury is swept with the pyrolysis gas and with an inert-carrier gas additionally fed to the system (the carrier gas is nitrogen in the concept considered here). The carrier gas with a high concentration of mercury is directed to a mercury separator, where Hg is extracted from the gas e.g., by adsorption in a fixed bed reactor (not included in the diagram). The flue gas from the pyrolysis reactor system is divided into two streams: one is recirculated to the system and the other cooled in a cooler (21), where the moisture contained in it is condensed and the heat recovered.

The cleaned coal is directed to a storage yard or directly to combustion (the most favourable option because of the use of the physical enthalpy of the hot fuel)

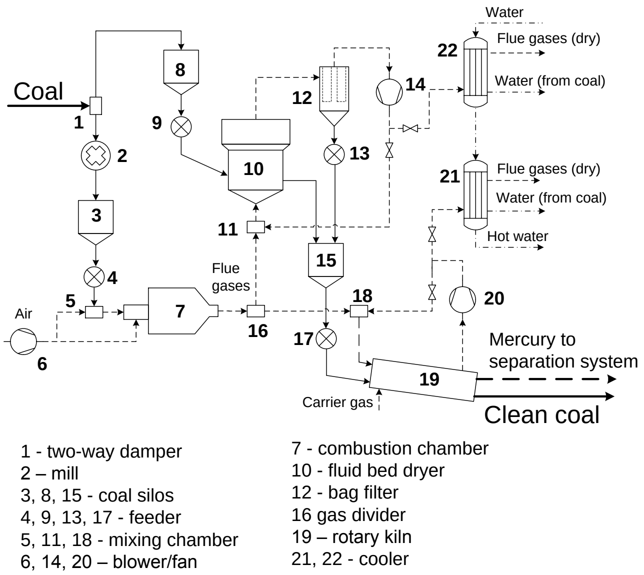

Fig. 2. Process diagram of a system for mercury removal from fuel using low-temperature pyrolysis.

4. MASS AND HEAT BALANCE

The mass and heat balance of the plant was determined based on the results of calculations carried out for the technological process presented in Fig. 2. The fuel composition (Table 1), plant capacity, yields of pyrolysis products (Table 2) and efficiencies of mercury removal were assumed in accordance with the results of studies on mercury distribution in industrial plants [1, 2] and laboratory research on pyrolysis [1]. The balance calculations were performed using the following assumptions:

- **Plant's Capacity**
  - hard coal: 50 t.p.h. of raw coal (thermal power in the fuel: 355 MW_{th}),
  - brown coal: 250 t.p.h. of raw coal (thermal power in the fuel: 804 MW_{th}).
- **Efficiencies of mercury removal from the fuel:**
  - hard coal: 60% ,
  - brown coal: 90%,
- temperature of pyrolysis = 300°C,
- fuel temperature after drying = 120°C,
- raw materials (fuel, air, carrier gas) temperature = 15°C,
- the loss of heat in dryer and pyrolysis systems: 5% of heat delivered to the system,
- flammable matter content in slag: 5%,
- temperature of fresh flue gas fed to the system = 1100°C,
- thermal efficiency of the combustion chamber: ~ 90%,
- annual availability of the plant: 85%.

Table 1
Hard and brown coal characteristics (as received)

Parameter	Unit	Hard coal	Brown coal
C	%	65,1	28,0
H	%	3,9	2,5
N	%	1,1	0,3
S_{total}	%	0,5	0,3
O	%	7,2	8,7
W_{total}	%	9,4	40,3
A	%	12,8	19,9
Hg	ppb	60	125
LHV[1)]	kJ/kg	25 534	11 572
HHV[1)]	kJ/kg	26 646	13 232

1) Calculated values; Dulong formula [10]

The mass and energy balance for hard and brown coal processing are presented in Figs. 3 and 4 and in Table 3.

The system for mercury removal from hard coal with a fuel capacity of 50 t.p.h. requires the delivery of 13.3 MW_{th} of heat to carry out drying and low-temperature pyrolysis. The hot flue gases originating from the combustion of an additional 1.9 t.p.h. of coal constitute the source of heat (which provides 3.8% of the coal stream from which mercury is removed). As a result of the process implementation, 44.3 t.p.h. of coal is obtained with a mercury content of around 27 ppb (assumed separation efficiency = 60%). The plant requires a power supply of 3593 MWh (electrical power – 0.48 MW_e).

Table 2
Yields of the pyrolysis products

Products	Unit	Hard coal	Brown coal
Char	%	97,7	88,3
Liquid products	%	1,8	5,7
Water	*%*	*1,8*	*0,3*
Organic phase	*%*	*-*	*5,3*
Gaseous products	%	0,6	6,0

To run the process using brown coal, it is necessary to deliver much larger amounts of heat, which apart from the process scale (assumed plant capacity of 250 t.p.h.) results from the increased demand for heat in the drying process (humidity of 40.3%).

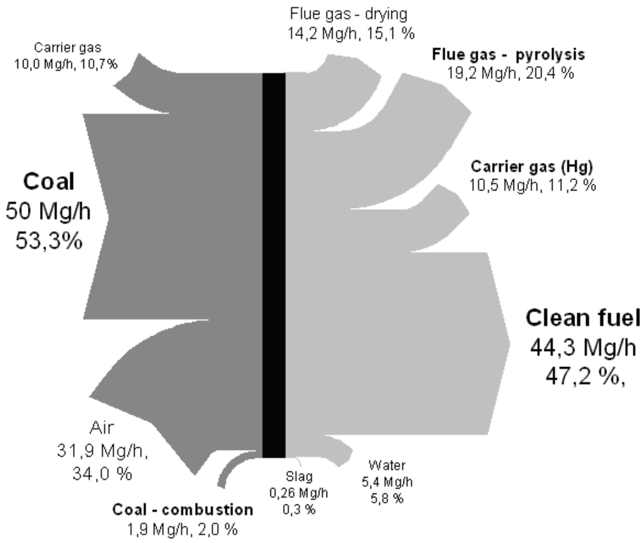

Fig. 3. Process mass balance of mercury removal from fuel using low-temperature pyrolysis; hard coal

As a result, to carry out drying and pyrolysis, it is necessary to deliver 128.6 MW_{th} of heat, which is obtained from burning an additional 40 t.p.h. of coal (16% of the coal stream, from which mercury is removed). Moreover, the plant requires a power supply of 31,841 MWh (electrical power – 4.28 MW_e). The obtained 126.8 t.p.h. of cleaned fuel contains a mercury concentration of 24.6 ppb (assumed separation efficiency is 90%).

The thermal efficiencies of the processes with respect to the cleaned fuel are 93.6% and 80.1%, respectively (Table 4). There is some potential in the field of process efficiency improvement, related mainly to the effective use of low temperature heat from flue gas cooling. Process optimisation would require a detailed analysis of the possibility of integrating the system with a power unit. The heat consumed during the removal of a unit amount of mercury from the fuel is 4.6 and 7.4 kJ/mg Hg for brown and hard coal, respectively. The 63% higher heat consumption for hard coal results from the much lower efficiencies of Hg removal under the assumed process parameters.

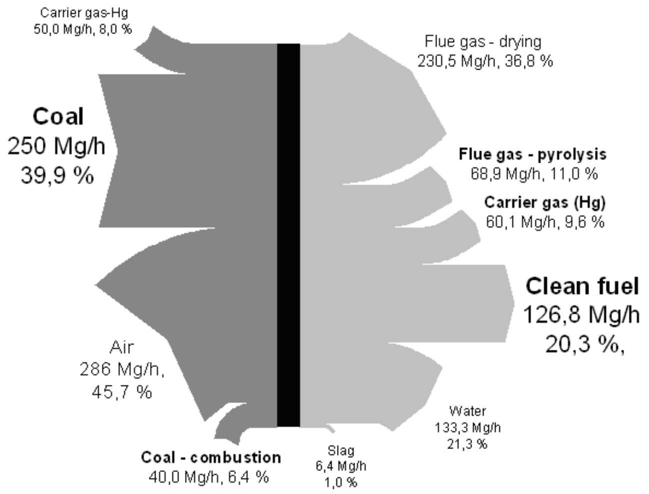

Fig. 4. Process mass balance of mercury removal from fuel using low-temperature pyrolysis; brown coal

Table 3

Energy balance of the process of removing mercury from the fuel using low-temperature pyrolysis (reference state t=25 ^oC)

No.	Stream	Hard coal				Brown coal			
		Chemical Enthalpy MW	Physical Enthalpy MW	Power MW	Total	Chemical Enthalpy MW	Physical Enthalpy MW	Power MW	Total
1	Coal	354,6	-0,15		354,5	803,6	-0,75		802,9
2	Coal - combustion	13,3	0,00		13,3	128,6	-0,12		128,5
3	Air		-0,09		-0,1	0,0	-0,80		-0,8
4	Carrier gas - Hg		-0,03		0,0	0,0	-0,14		-0,1
5	Power			0,5	0,5			4,3	4,3
	Total	**368,0**	**-0,27**	**0,5**	**368,2**	**932,2**	**-1,8**	**4,3**	**934,7**
6	Cleaned fuel	344,5	4,86		349,4	748,5	13,93		762,4
7	Carrier gas - Hg	0,8	0,06		0,8	15,8	0,30		16,1
8	Flue gas- pyrolysis		0,10		0,1		0,36		0,4
9	Flue gas- drying		0,07		0,1		1,19		1,2
10	Slag		0,10		0,1		2,45		2,4
11	Low temperature heat		5,64		5,6		105,38		105,4
12	Losses (by difference)				12,1				46,7
	Total	**345,3**	**10,8**	**0,0**	**368,2**	**764,3**	**123,6**	**0,0**	**934,7**

Table 4
Thermal efficiency of the process of removing mercury from the fuel using low-temperature pyrolysis

No.	Case/product	Hard coal	Brown coal
		%	%
1	Clean fuel (hot) and low temperature heat	96,4	92,8
2	Clean fuel (hot)	94,9	81,6
3	Clean fuel (cold/ambient temp.)	93,6	80,1

Solid, liquid and gaseous products are obtained through the process. Mostly due to water loss, the elemental composition of the refined fuel changes and exhibits a higher calorific value than raw coal (increase of 13.5% and 86% for hard and brown coal, respectively). The pyrolysis gas generated in the process has a calorific value of approximately 11 and 6.6 kJ/kg for hard and brown coal, respectively (this value is calculated for a nitrogen-free state; [1]). This gas is removed from the reaction system by means of a carrier gas (nitrogen). The calorific value of the gas transporting mercury to the adsorption system (carrier gas) is low and amounts to 263 and 940 kJ/kg for hard and brown coal, respectively, due to a small stream of pyrolysis gas. In both cases, the share of flammable components of the gas is approximately a fraction of a percent. The carrier gas also removes liquid products from the system.

In the case of hard coal, pyrolysis liquid products consist mainly of water, which is removed from the system before adsorption. However in the case of brown coal, also the organic fraction (tar) is present. The organic fraction may be fired in a boiler after being separated from water, increasing the thermal efficiency of the process.

The separated mercury is extracted from the system in gaseous products of the process (with the inert). A high mercury concentration is obtained as a result of a relatively small stream of pyrolysis and carrier gas; this mercury may be separated, with high efficiency and at relatively low cost by adsorption in a fixed bed reactor. The stream of carrier gas constitutes only approximately 1.6% and 3.6% (for hard and brown coal, respectively) of the stream of flue gas, originating from the combustion of coal, subject to Hg removal by means of secondary methods. The Hg concentration in the carrier gas is approximately 25 to 35 times higher than in the flue gas.

5. SUMMARY

The issue of reducing the emission of heavy metals, especially mercury, into the environment has raised a growing interest in Europe and around the world, which is reflected in administrative and legislative activities and research and development efforts. Special attention is paid to coal combustion processes for power production as they are the main source of mercury emissions in the atmosphere. The introduction of mercury emission standards in the coal-fired power industry will, in most cases, result in the necessity to implement additional technologies to clean flue gases. Apart from the best commercially developed technologies related to sorbent injection, other technological solutions are worth considering, including mercury removal from fuel prior to its combustion via thermal treatment.

The research carried out at the ICPC on a laboratory scale has demonstrated the possibility of substantially reducing mercury content in coal (65% and 94% for hard and brown coal, respectively) through pyrolysis at a temperature of 300°C and residence times of 10-20 min.

The analysis of the concept of low-temperature pyrolysis implementation on a commercial scale demonstrates the technical feasibility of the process.

Further work is necessary to obtain a full assessment of the studied process, including the verification of the experiment results on a large laboratory/pilot scale and detailed technical-economic analyses to reliably determine the costs of mercury removal with the use of the suggested technological solution. Due to much lower values of the gas stream versus the flue gas from which mercury is separated, the process is relatively easy to implement and may turn out to be cost competitive). The research will be continued under the strategic project “Advanced technologies for energy acquisition – Development of coal gasification technology for highly efficient production of fuels and electricity”. The goal of the future work will be the development and testing of a technology for mercury removal from coal using low-temperature pyrolysis in a rotary reactor (continuous process) on a large laboratory scale.

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OBNIŻENIE EMISJI RTĘCI DO ATMOSFERY Z PROCESÓW SPALANIA WĘGLA Z WYKORZYSTANIEM PIROLIZY NISKOTEMPERATUROWEJ – KONCEPCJA REALIZACJI PROCESU W SKALI PRZEMYSŁOWEJ

Słowa kluczowe: rtęć, węgiel, piroliza, ograniczenie emisji

Streszczenie. W artykule zaprezentowano wyniki badań usuwania rtęci z węgla przed procesem spalania na drodze pirolizy niskotemperaturowej oraz koncepcję realizacji procesu w skali przemysłowej. Dla zaproponowanej konfiguracji układu opracowano bilanse masowe i energetyczne instalacji. Koncepcja technologiczna układu zakłada, że będzie się on składać z dwóch podstawowych węzłów technologicznych tj. suszenia i pirolizy a nośnikiem ciepła będą spaliny otrzymane ze spalenia dodatkowej ilości węgla. Sprawność realizacji procesu, zdefiniowana jako stosunek entalpii chemicznej produktu (tj. węgla oczyszczonego) do entalpii paliwa surowego, waha się w zakresie od 80% do 94% dla węgli brunatnych i kamiennych. Ze względu na dużo niższe wielkości strumienia gazu (w stosunku do spalin), z którego separowana jest rtęć, proces jest stosunkowo łatwy w realizacji i może okazać się konkurencyjny kosztowo. Nie powoduje również ingerencji w istniejące układy technologiczne elektrowni.

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