



národní
úložiště
šedé
literatury

Concentration of HCl, HF and Sulfur Compounds in Fuel Gas from Fluidized Bed Gasification of Coals and Wood by Steam-Oxygen Mixtures

Svoboda, Karel
2012

Dostupný z <http://www.nusl.cz/ntk/nusl-126636>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

Tento dokument byl stažen z Národního úložiště šedé literatury (NUŠL).

Datum stažení: 20.06.2024

Další dokumenty můžete najít prostřednictvím vyhledávacího rozhraní nusl.cz .

Concentration of HCl, HF and sulfur compounds in fuel gas from fluidized bed gasification of coals and wood by steam-oxygen mixtures

¹Karel Svoboda, ^{1,2}Michael Pohořelý, ^{1,2}Michal Jeremiáš, ¹Petra Kameníková,
³Siarhei Skoblja, ³Zdeněk Beňo, ¹Michal Šyc

¹ Institute of Chemical Process Fundamentals of the ASCR, v.v.i., Rozvojová 135,
165 02 Prague 6, Czech Republic, Tel.: +420 220 390 241, Fax: +420 220 920 661 ,
E-mail: svoboda@icpf.cas.cz

² Dep. of Power Engineering, Institute of Chemical Technol., Technická 5, 166 28 Prague 6

³ Dep. of Gas, Coke and Air protection, Institute of Chemical Technol., Technická 5,
166 28 Prague 6, E-mail: sergej.skoblja@vscht.cz

Key words: Fluidized bed, gasification, coal, biomass, HCl, HF, H₂S, thiophene

1. Introduction

Syngas produced by a gasification process of coals and biomass fuels can be used for production of electricity, hydrogen, synthetic transportation fuels and other chemicals. The advanced utilization of syngas is significantly limited due to the contaminants which can seriously deactivate the catalysts used for downstream reactions (steam reforming, Fischer–Tropsch synthesis) and cause corrosion and damage of downstream equipments such as a gas turbine or high temperature fuel cells. Among the gas contaminants, sulfur compounds, HCl and HF produced in the gasification process¹⁻⁵ belong to the most dangerous, which must be removed or substantially decreased for various gas end-users.

In fluidized bed (FB) gasification a partial reduction of HCl, HF and sulfur compounds concentrations in fuel gas can be done by limestone or dolomite based in-bed particulate materials⁶⁻⁸. Water vapour concentration plays a significant role in equilibrium reactions with lime-based sorbents⁹. Accumulation of ash/char in FB, presence of fly ash in the freeboard (above the dense FB) and ash composition are also important factors^{10,11}.

In the case of sulfur compounds the main attention is usually focused on H₂S removal¹²⁻¹⁴, but for deactivation of reforming/tar destructing catalyst downstream fuel gas desulfurization by solid sorbents (e.g. ZnO based) presence of other sulfur compounds (COS, CS₂, thiophene, benzo-thiophene) is very important^{3,5}.

Biomass (particularly wood) has advantage in lower content of sulfur, chlorine and nitrogen in comparison with coal. The herbaceous biomass (straw, grass etc.) can have, however content of chlorine, sulfur and nitrogen comparable or even higher than some coals^{2,3,11,15}.

In-bed retention of sulfur, chlorine and fluorine is a complex function^{2,11,15} of presence (forms and concentrations) of Na, K, Ca, Fe in ash (in additives) and depends to a considerable extent on interactions of the halide and sulfur sorbents with ash components (SiO₂, Al₂O₃, kaolin etc.), on presence of melted eutectics, on water vapour and CO₂ partial pressures. CaO is more reactive towards HCl, HF and H₂S than CaCO₃^{2,15} and also the equilibria are more favourable for deeper removal of the mentioned gaseous impurities.

The analytics of sulfur compounds and their speciation requires GC based modern methods with special, sensitive and selective sulfur detection SCD^{5,16}. For HCl and HF

determination in absorption water solutions mostly ion electroforesis or ion chromatographic methods are used nowadays^{10,16,17} .

We have concentrated in our study on FB gasification of two kinds of coals differing in reactivity, ash content and composition (reactive, sub-bituminous coal and bituminous less reactive coal) and hard wood at temperature 850 °C. Our attention was particularly devoted to speciation of sulfur compounds (H₂S, COS, CS₂, thiophene), presence of HCl, HF and tar compounds in fuel gas. Silica sand and mixture of silica sand with gradually added dolomite was used as basic particulate bed material in FB gasification.

The results have shown that presence of dolomite particles in the fluidized bed and presence of dolomite dust (from attrition) reduces concentrations of all sulfur species, but the reduction of thiophene concentration is more pronounced. Presence of dolomite in FB causes substantial decrease of HCl concentration and moderate decrease of HF concentration in fuel gas. Accumulation of char and ash with active calcium based components leads to moderate reduction of HCl and sulfur compounds concentration in fuel gas. On the other hand, the increase of H₂O concentration in gas contributes through hydro-pyrolysis of CaCl₂ to the elevation of HCl concentration.

Reactivity of coal, content of ash and content of alkalis in ash are very significant factors in carbon loss from FB gasification of coal and for tar content/composition. Biomass (wood) is usually more convenient for FB gasification because of high content of volatiles exceeding 80 mass % of combustibles and lower carbon loss in dust.

The in-bed measures for abatement of HCl, HF and sulfur compounds concentrations are still insufficient from the point of view of requirements of catalytic processes and fuel cells (SOFC) applications and therefore downstream deep cleaning methods for fuel gas have to be applied^{18,19} .

2. Experimental

2.1 Fuels and dolomite used for gasification

The three fuels used for FB gasification experiments are compared in **Table I**. The German sub-bituminous coal is low ash coal (3.9 mass % of ash) with relatively high content of volatile combustibles. The South African coal is rather typical bituminous coal with lower content of volatiles. In comparison with the coal, wood has naturally higher content of volatiles. As the basic FB particulate inert material, the particles of quartz sand (0.25 – 0.5 mm) have been used. In selected experimental runs (German coal), effects of addition of dolomite to the sand on gas composition has been studied. Properties and composition of the dolomite used are summarized in **Table II**.

Comparison of coal ash compositions of the two coal and composition of wood ash is shown in **Table III**.

Table I: Composition of German (subbituminous) coal, South African (bituminous) coal and ground wood

Components (mass %)	German coal	South African coal	Ground wood
Water (raw)	11.3	5.9	9.8
Ash (raw)	3.9	10.7	0.9
Combustibles (raw)	84.8	83.4	89.3
Volatiles (daf)	51.65	31.3	83.54
Fixed carbon (daf)	48.35	68.7	16.46
C (daf)	66.2	79.71	49.16
H (daf)	5.07	4.68	6.05
O (daf)	27.12	13.18	44.79
N (daf)	0.84	2.01	0.19
S (daf)	0.354	0.45	0.022
Cl (daf)	0.0472	0.0240	0.0111
F (daf)	0.00472	0.0156	0.00336
Particle size (mm)	0.5 – 2.0	0.5 - 2.0	0.5 – 2.0
Mean particle size	1.25	1.25	1.25
LHV - raw fuel (MJ/kg)	21.85	25.64	16.08

Table II: Particle properties and chemical composition of the dolomite used

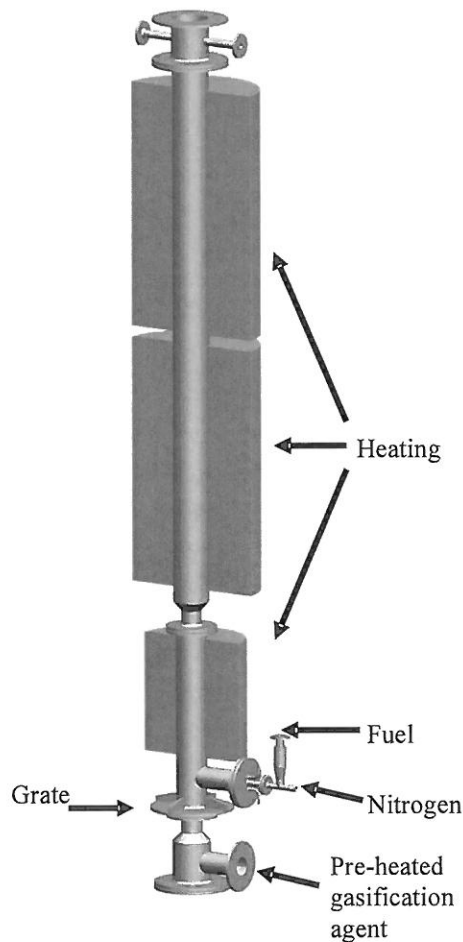
Particle size - raw (mm)	0.5 – 1.25	CaO (calcine)	65.89 mass %
Mean particle size (mm)	0.75	MgO (calcine)	33.24 mass %
Apparent density (calcine)	1150 kg/m ³	Fe ₂ O ₃ (calcine)	0.047 mass %
True (He) density (calcine)	2946 kg/m ³	SiO ₂ (calcine)	0.359 mass %
Porosity (calcine)	0.61	Al ₂ O ₃ (calcine)	0.29 mass %
U _{mf} (25 °C, calcine)	0.21 m/s	Loss on ignition, raw dolomite	46 mass %

Table III: Chemical composition of ash from the German coal, South African coal and wood

Element (oxide)	German coal (mass %)	South African coal (mass %)	Ground wood (mass %)
CaO	42.25	3.21	35.0
MgO	20.63	0.79	5.42
Fe ₂ O ₃	14.10	2.97	5.39
SO ₃ (after oxid.)	10.98	1.98	4.8
Na ₂ O	4.68	0.420	0.03
Al ₂ O ₃	4.61	36.38	5.34
SiO ₂	0.87	49.27	5.61
K ₂ O	0.623	0.73	24.0
SrO	0.357	0.36	
TiO ₂	0.244	1.69	0.054
MnO	0.2	0.035	1.27
Cl	0.012		0.05
P ₂ O ₅	0.0131	1.51	13.0

2.2 Experimental facility for FB gasification and feeding of fuels

Gasification experiments were carried out in the atmospheric FB reactor, which is schematically shown in **Fig. 1**. The reactor is made of high-temperature resistant stainless steel with the maximum operating temperature of 1000 °C. Upstream to the reactor itself, there is a gas mixing device supplied by Bronkhorst HI-TEC, which is used as a generator of gasification agent of precise composition. Gasification agent can be heated up to 800°C in an electrical pre-heater before entering the FB reactor.



The main part of the reactor, the reaction zone, is an electrically heated 2200 mm high tube with the inner diameter of 51.1 mm in the lower section and 99.0 mm in the upper section. Size reduction is placed in the height of 540 mm above the grate. The fuel particle feeding line is shown in **Fig. 2**. The feeding line consists of a two chamber PTFE slide feeder with consequent pneumatic transport by means of N₂. The feeding rate can be controlled by dimensions of the cylindrical chambers and by variable frequency of the sliding plate with two chambers (holes). Detailed description of the dosing device can be found elsewhere^{20,21}. The feeding line was cooled by a water cooler at the entrance to the FB reactor (gasifier). The axis of the fuel feeding pneumatic transport tube is about 40 mm above the gas distributor.

The volumetric flow rates of oxygen and of both N₂ for pneumatic transport and gasification agent were controlled by mass flow controllers. Electrical heating consists of three independent sections along height of the reactor. Design of the heating system enables to control the temperatures in three reactor zones independently. The temperatures in denser FB and in freeboard are measured directly in the axis of the reactor by K-type thermocouples.

Fig. 1: Scheme of experimental facility

In the top part of the reactor, outlets are placed for pressure monitoring and sampling for off-line gas analysis and tar content determination in the producer gas. The hot raw producer gas is dedusted in a cyclone working at 400–500°C. Producer gas is further sampled for on-line analysis of major components and fed to the exhaust. The gas for analyses of sulfur compounds, HCl and HF was sampled behind cyclone.

In the case of addition of dolomite particles for in-situ tar abatement and partial sorption of HCl, H₂S and HF in fuel gas the dolomite particles (0.5 – 1.25 mm) were fed to the reactor from the top with batch feeding frequency 223 g/h (procedure used for German coal).

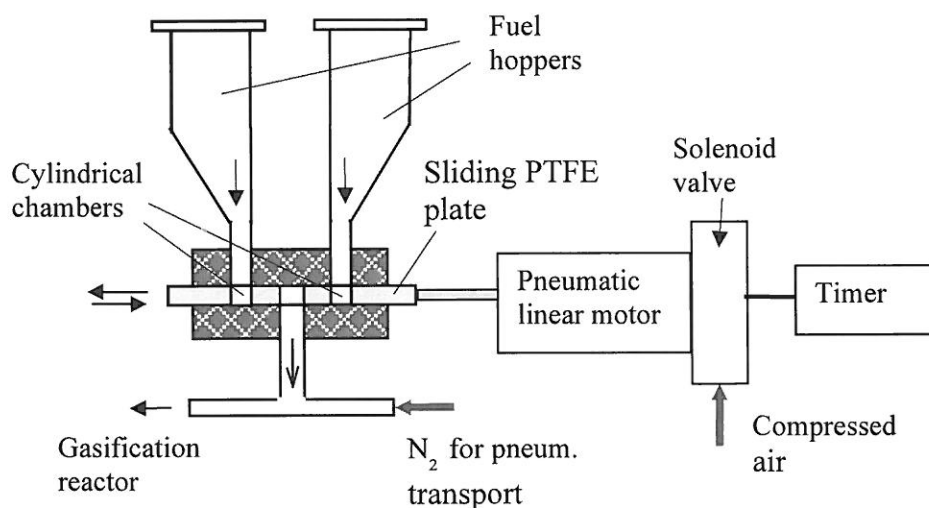


Fig. 2 : Scheme of the double-acting, compressed air driven slide feeder²¹ with interchangeable sliding plate provided with two cylindrical holes (chambers)

2.3 Producer gas analysis

2.3.1 Major and minor gas analysis and tar analysis

Producer gas was analyzed both on-line and off-line. On-line analysis served for monitoring and control of the gasification process and off-line analysis supplied data for a detailed study of gasification products. Major gas components (CO, CO₂ and CH₄) were analysed on-line by means of ND-IR analyzers.

The presented gas composition data are based on the off-line GC analysis of the producer gas (gas chromatograph HP 6890 equipped with two analytical channels). The details of the GC analyses for gas components can be found elsewhere²⁰. A standard sampling line was used for tar collection according to the Tar protocol^{22,23}. For our purposes we used three absorption bottles with acetone (150 ml). The first one was at a normal temperature, the other two were cooled in a bath with solid CO₂ (−70 °C). Tar components were analysed by the gas chromatograph HP 6890 with mass selective detector MSD 5973. The tar components were identified by comparing them with NIST mass spectra library and with the retention data of the available standards solution. The quantification was done from standard solutions measured under the same conditions.

2.3.2. Determination of sulfur compounds in producer gas

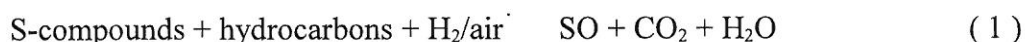
In principle, H₂S, COS, CS₂, thiophene, benzo- and dibenzo-thiophene can be present in fuel gas from gasification of solid fuels containing sulfur. The main sulfur components in producer gas are, however, mostly H₂S, COS and thiophene.

The basic characteristics of flame photometric detector (FPD), pulse flame ionization detector (PFPD), sulfur chemi-luminescence detector (SCD), atomic emission detector (AED) and electron capture detector (ECD) are compared for sulfur compounds detection in **Table IV**.

Table IV: Comparison of basic characteristics of selective detectors for quantitative determination of sulfur compounds

Detector	MDL (pg/s)	Linearity	Selectivity	Dependence of response on structure of a compound
FPD	20	Quadratic prop.	1×10^5	Yes
PFPD	0.5 - 1	Quadratic prop.	1×10^7	No
SCD	0.5	1×10^5	1×10^6	No
AED	2	2.0×10^4	1.5×10^5	No
ECD	limit [0.005	1×10^4	Depends on electro-negativity of elements in given molecule	Yes

Because of excellent properties (MDL, linearity, selectivity) we decided for the SCD detection. The SCD can be used for detection of various sulfur compounds in gas. Moreover, there is no interference from the side of water vapour and CO₂. The principle of SCD is based on conversion of sulfur compounds to sulfur monoxide (SO) in reduction flame:



Reaction of SO with ozone (in a reaction cell at mild vacuum) leads to excited molecule SO₂*:



The excited SO₂ molecule returns to the basic state by emitting chemi-luminescence radiation in wave-range 260 – 480 nm:



The output signal is not dependent on sulfur compounds structure.

The new SCD detector generation has double plasma-burner (electrically heated up to 800 °C) with oxidation and reduction zone. Sensitivity of such an arrangement leads also to higher sensitivity of sulfur detection.

We have used the GC Agilent 7890 A with the modern conception of SCD detector Agilent 355 with dynamic dilution system of gas samples for preparation of gaseous mixtures with low concentrations of sulfur compounds.

Analytical capillary column DB-1, length 30 m, inner diameter 0.32 mm, thickness of the film 1 μm, constant He flow rate (2 ml/min.) was used for GC. Flow rates into double plasma burner were regulated by EPC modules: air: 320 kPa (about 56 cm³/min) and hydrogen: 189 kPa (about 42 cm³/min). Temperature program of GC began on 30 °C, heating rate 20 °C/min up to 80 °C (2 min. delay). In the case of input of liquid samples with high boiling points compounds the heating continued up to 320 °C (delay 3 minutes).

The linearity of SCD output signal was confirmed for varying ratio of THT, thiophene and methylthiophene. The output signal is, therefore independent on nature (composition, structure) of sulfur compounds.

Tar compounds (sampled according to the Tar protocol) exerted contents of heavier sulfur compounds. The gas chromatogram (GC-SCD) is shown in **Fig. 3**. Tar contents various sulfur compounds, mostly thiophene and its alkylated compounds, benzothiophene (+its alkylated compounds) and dibenzothiophene (+ its alkylated compounds). For exact

identification and quantitative determination of sulfur compounds in gas and tar the samples of pure substances (standards for calibration) are needed.

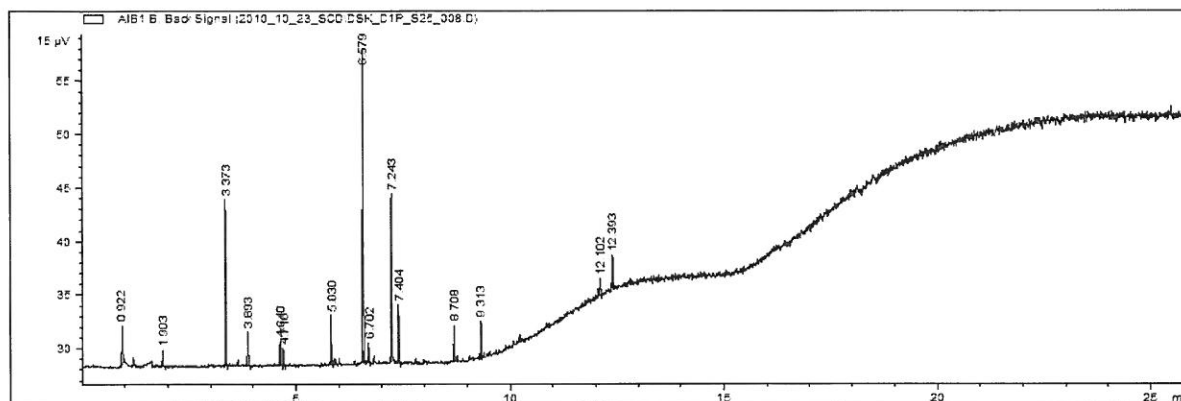


Fig. 3: GC-SCD chromatogram of sulfur containing tar compounds from producer gas (gasification of wood).

The producer gas from gasification of coals contains significantly more sulfur and beside the H_2S also concentrations of COS, thiophene, benzo-thiophene and CS_2 (in small extent) can be found.

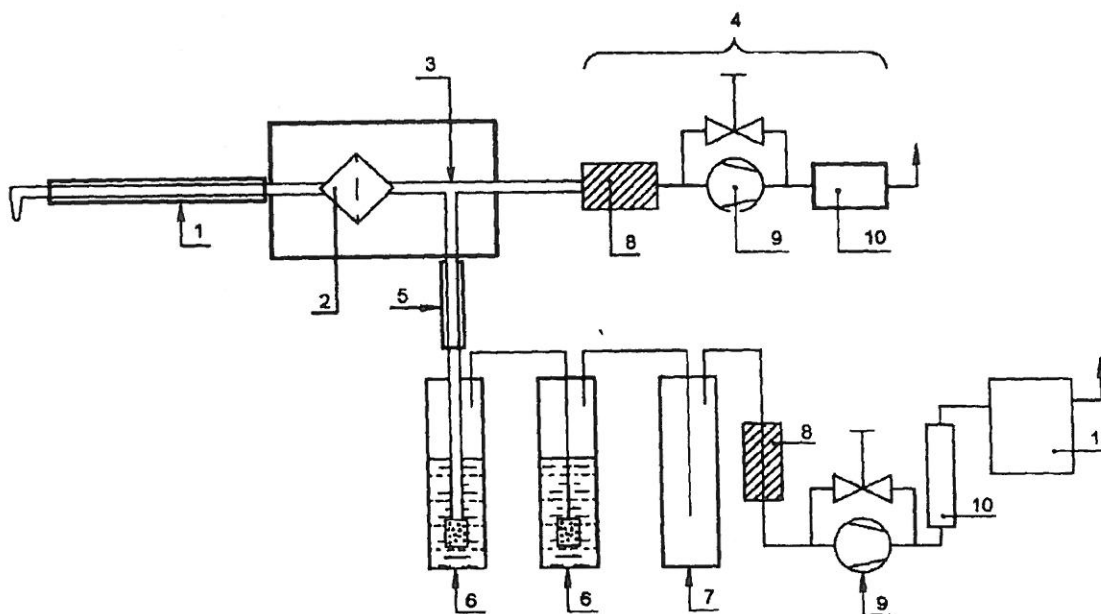
The sampling point of producer gas for H_2S determination was behind the hot cyclone, without additional fine filter and the gas was led through a bubble bottle filled with diluted sulfuric acid (to eliminate interferences cause by simultaneous presence of NH_3 and H_2S in the sampled gas) into Tedlar bag (3 l volume). The diluted sulfuric acid decomposed the formed ammonium salts (ammonium sulfide) and bound all ammonia. The concentrations of H_2S found downstream the diluted sulfuric acid solution in the sampling line can be considered as more reliable. For determination of the sulfur compounds sampling through the top lid of the FB reactor was used, without fine filter, directly to the Tedlar bag.

2.3.3 Determination of HCl and HF content in producer gas

There are several procedures for quantitative determinations of HCl and HF concentrations in producer gas. We will concentrate here mainly on off-line method based on absorption of gas samples and determination of the halogens in liquid samples. The EU norms (EN) and corresponding Czech norms (ČSN) are applied 24-25 for determination of chlorides and HCl in waste gases. These norms are applicable for gases containing HCl in mass concentration range $1 \text{ mg/m}^3 - 5\,000 \text{ mg/m}^3$. This method allows determination of all chlorine compounds volatile at temperature of gas filtration and soluble in absorption liquid (volatile chlorides expressed as HCl). The main (decisive part) of the chlorides is usually in the form of HCl (very small part can be in a form of aerosol particles of solid chlorides or chlorinated organic compounds). If necessary a more precise speciation of chlorine based volatile compounds can be considered and performed.

Sampling of gas should be downstream the hot cyclone for elimination of bigger particles from gas. The fine filter in the sampling line should operate at temperatures with only small or negligible tar compounds condensation. The tubing should be short. An example of sampling system is shown in Fig. 4. If a small condensation is present in sampling system a water flushing is needed. The flushing water is added to absorption water (liquid) [24]. In presence

of BTX and tar compounds in gas, formation of drops, liquid film or precipitation of particles in absorption water is possible. Absorbing water solution (diluted, 0.1 M NaOH solution) should be based on pure water and NaOH without chlorides. Absorption line can involve also a safety empty bottle for capture of escaping liquid from absorption bottles [25]. The absorption solution was analyzed by ion chromatography and in few cases checked by argentometric titration with potentiometric indication of the equivalent point.



1 - heated sampling tube with inlet tip	6 - washing (absorption) bottle
2 - heated particle filter	7 - safety (empty) bottle
3 - heated T-piece	8 - gas dryer
4 - unit for gas sucking	9 - gas pump
5 - heated connecting tube	10 - gas flow rate measurement

Fig. 4: Example of sampling line for HCl absorption from producer gas

The choice of the analytical method depends mainly on supposed concentration range of chlorides (on concentration of HCl in analyzed producer gas, on absorption time and on volume of absorption water solution). Detailed procedure for all of the mentioned methods and chemicals needed are stated in EN 1911-3 [26].

We have used for determination of chlorides and fluorides in diluted (0.1 M) water-NaOH solution ion chromatography. For determination of only HCl in fuel gas absorption into pure (de-mineralized) water can be used.

Determination of HF in fuel gas was performed in accordance with the norms 17,27 . The absorption solution (0.1 M water solution of NaOH) was common for simultaneous HCl and HF determination.

Instrumentation – ion chromatography

All samples were analyzed using DIONEX ICS-5000 Ion Chromatography (IC) System equipped with IonPac CS18 analytical (2x250mm) column and a guard column for analysis of cations and IonPac AS11-HC and a guard column for analysis of anions. The system enables parallel analysis of anions and cations due to dual system of ICS-5000 Conductivity Detectors

(CD) and dual high pressure analytical pumps - one gradient (cation branch) and one isocratic (anion branch). The system works in suppressed conductivity mode being equipped with anion self-regenerating suppressor ASR® 300 2mm in anion branch and cation self-regenerating suppressor CSRS® ULTRA II, 2mm working in autosuppression® recycle mode. Moreover, anion branch is equipped with an eluent generator cartridge with potassium hydroxide RFIC eluent generator that enables stable and CO₂ free eluent concentration. Cation eluent is water solution of methane sulfonic acid.

Anion analysis is done using flow rate 0.38 ml/min of 30 mmol KOH at temperature 30°C, suppressor is set to 29 mA at temperature 35°C. Cation analysis used flow rate 0.25 ml/min of 5 mmol methanesulfonic acid, and suppressor was set to 6 mA. In both cases the sample volume injected into the analytical column was 25 µl. One analysis took 20 min in both cases.

Calibration

An external calibration is used during all analytical runs. The seven levels of concentrations of calibration solution were used, from 25 ppm down to 0.25 ppm. Fluoride, chloride, nitrite, sulfate, bromide, nitrate and dihydrogen-phosphate were calibrated within anions. Sodium, ammonium, potassium, magnesium and calcium were calibrated within cations. Both calibration solutions were prepared from NIST traced commercial calibration solutions using calibrated micro pipettes and ultrapure water. To check stability of the suppression system one level of calibration solution was measured at least twice during analytical run.

Sample analysis

The real samples were obtained by absorption of producer (fuel) gas pollutants in water (HCl only) or diluted NaOH solution (HF + HCl). This approach in connection with gasification technology leads to higher content of organic species in solution or even to formation of second phase that may be both liquid and solid. These effects may negatively influence the analytical procedures. Therefore, the analytical procedures were first tested using artificially prepared standardized samples that were prepared by using known amounts of analytes. Naphthalene, toluene and anthracene were added into a solution of 0.1 mol H₂SO₄ or 0.1 mol NaOH and the analyzed species (F⁻, Cl⁻, Br⁻ and NH₄⁺). Due to high concentration of basic solutions the samples has to be diluted 10-100 times. Nevertheless, the reasonable agreement between analyzed and premixed concentration was found. The analyses have been more reliable with more diluted water solution samples – it means that absorption into 0.02 M or 0.01 M solutions (instead of 0.1 M solution), if possible, should be preferred.

The real samples were analyzed within 2 weeks from the date of an experiment. The samples were stored in a fridge before the analyses. The samples were diluted before the analysis, they were filtered using a PVDF syringe filter with 0.22 µm pore size to remove any larger particles and analyzed using Dionex ICS-5000 ion chromatography system. Besides real samples, all the solutions used for flue gas scrubbing were analyzed and the same was done with ultrapure water used for sample dilution. The concentration of all analyzed species before dilution was determined and the results were passed on for their evaluation. Some of the samples have been analyzed by Ag-metric method for checking. The conformity of the results from both methods was relatively good, particularly at lower content of organics.

The preliminary results from analyses of volatile, water soluble chlorides and fluorides show that degree of dilution and presence of excess PAH compounds can play some role in precision of determination of Cl⁻ and F⁻ anions. The determined concentrations of chlorides and fluorides (HCl and HF) in fuel gas from FB gasification with O₂/H₂O mixtures (ER = 0.2, molar H₂O/C > 1) are below 20 mg/m³ in sampled gas and below 6 mg/m³ respectively. The conversions of fuel Cl and F into water soluble, volatile chlorine and fluorine compounds

(mainly HCl and HF) is below approx. 15 %. The analyses of very small bromine contents in coals and in producer gas are still problematic and unsure.

2.4 Experimental condition for the FB gasification

The experimental conditions for the FB gasification of the German coal, South African (SA) coal and biomass (wood) in the FB of sand particles are given in **Tables V** and **VI**. The fuels have been gasified by water vapour-oxygen mixtures. Nitrogen served as inert gas for pneumatic transport and for maintaining the desired fluidization velocity. The samples of gas for GC analyses have been taken at steady state FB gasification at 850 °C – used generally as the basic reference temperature. Quartz sand served as the basic FB particulate material.

Table V: Experimental conditions for FB gasification of German coal and South African coal at 850 °C (initial FB material: sand)

Material of fluidized bed	Quartz sand 0.25 – 0.5 mm	
Gasification agent	Steam + oxygen	
Measurements	Gas compos., HCl, HF, tar, sulfur compounds	
Coal (raw) feeding rate (g/h)	1207 (G-coal)	1145 (SA coal)
Water vapour	1000 g/h, 1.36 m ³ /h	1.36m ³ /h 1001 g/h
Nitrogen for gasification G-coal and SA-coal	0.34 m ³ /h	0.3 m ³ /h
Nitrogen for pneumatic transport	1.5 m ³ /h	1.5 m ³ /h
Oxygen (G-coal, SA-coal)	0.32 m ³ /h	0.34 m ³ /h
Basic H ₂ O/dry fuel mass ratio and molar H ₂ O/C basic molar ratio (G-coal, SA-coal)	1.07 kg/kg Molar ratio: 1.13	0.99 kg/kg 0.94
Equivalent oxygen/fuel ratio ER	0.21 (G-Coal)	0.20 (SA-coal)
Reactor temperature	850 °C	850 °C
Approx. content of N ₂ in dry producer gas	G- coal: approx. SA-coal:	45-50 vol. % 60-66 vol. %

Table VI: Experimental conditions for FB gasification of wood (FB material: sand)

Material of fluidized bed	Quartz sand 0.25 – 0.5 mm	
Overall length of gasification experiment	about 6 hours	
Gasification agent	steam + oxygen	
Measurements	Gas compos., HCl, HF, tar, sulfur compounds	
Wood (raw) feeding rate (g/h)	1417	
Water vapour	1001 g/h,	1.36 m ³ /h
Nitrogen for gasification	0.33 m ³ /h	
Nitrogen for pneumatic transport	1.2 m ³ /h	
Oxygen	0.32 m ³ /h	
Basic H ₂ O/dry fuel mass ratio	0.89 kg/kg	H ₂ O/C molar ratio = 1.22
Equivalent oxygen/fuel ratio ER	0.25	
Reactor temperature	850 °C	
Approx. content of N ₂ in dry prod. gas	53.7 - 55 vol. %	

The experimental measurements with sand and batch additions of dolomite particles into FB (**Table VII**) have been performed only for German coal gasification. Batch doses (223 g) of raw dolomite were added every hour to the initial quartz sand bed (750 ml).

Table VII: Experimental conditions for FB gasification of German coal with additions of dolomite (quartz sand + dolomite)

Material of fluidized bed	Quartz sand 0.25 – 0.5 mm (additions of dolomite 0.5 – 1.25 mm)
Gasification agent	Steam + oxygen
Measurements	Gas compos., HCl, HF, tar, sulfur compounds
Coal (raw) feeding rate (g/h)	1303
Water vapour	1001 g/h, 1.36 m ³ /h
N ₂ for gasification G-coal and SA-coal	0.31 m ³ /h
Nitrogen for pneumatic transport	1.5 m ³ /h
Oxygen (G-coal, wood)	0.33 m ³ /h
H ₂ O/dry fuel mass ratio and H ₂ O/C molar ratio (G-coal, wood)	1.02 kg/kg Molar ratio: 1.07
Equivalent oxygen/fuel ratio ER	0.21
Reactor temperature	850 °C
Mass of raw dolomite in the bed	batch additions, 223g/h
Approx. content of N ₂ in dry producer gas	Approx.: 40 - 44 vol. %

3. Results and discussion

3.1 Comparison of HCl, HF and S-compounds emissions in gasification of SA coal, German coal

The conditions of FB gasification of SA-coal were: temperature 850 °C, ER = 0.20, molar H₂O/C ratio [1, coal particles size 0.5 – 2 mm. Time trends of HCl, HF and S-compounds concentrations and the conversions are shown for the SA coal in **Table VIII**. The time trends of HCl, FF and S-compounds concentrations (together with the corresponding conversions) for German coal gasification are given in **Table XI**.

The time trends of S-compounds and HCl (or HF) are different in the case of SA coal. While the S-compounds (mainly H₂S) concentrations decrease with increasing time of gasification, the HCl concentrations in gas increase substantially with time (**Table VIII**). According to estimated carbon balance during the gasification process, over 50 % of coal carbon remains as char in the gasifier. It means that the coal is far less reactive in gasification than the German coal, where the carbon content in the bed is much lower. The ash composition of the SA-coal (**Table III**) indicates that SiO₂ + Al₂O₃ are the prevailing components of ash (over 85 mass %) and the contents of alkali- and alkali earth metals are relatively low. Tar concentration (Total tar – BTX) drops very steeply with increasing time of gasification for gasification of both coals. The heavier tar concentrations are, however, significantly higher for the SA coal than for FB gasification of the German, subbituminous coal.

The reasons for increasing HCl concentrations in dry raw fuel gas from SA coal gasification are not clear. May be formation of low melting point temperature CaCl₂ based eutectics (with CaO, CaS, CaF₂, Fe-compounds, etc.) and reactions of the melts with SiO₂ (leading to formation of calcium silicates and volatilization of HCl) could be responsible for this time trend [2,8,28]. In the case of German coal gasification, the HCl, HF and sulfur compounds concentrations decrease with increasing time of gasification probably due to accumulation of char and ash with relatively high content of reactive CaO and alkali metals (Na, K). The conversions of fuel chlorine and fluorine to volatile HCl and HF are relatively low (3-14 %), but the conversions of fuel-S to sulfur compounds are relatively higher (22-66 %) for both coals gasified.

Table VIII: Comparison of emissions of HCl, HF, sulfur compounds, BTX and heavier tar compounds concentrations in FB gasification of SA (bituminous) coal on sand particles

South African coal (SA coal)			
	raw (wt)	dry (wt)	
Cl	0.02%	0.02%	
F	0.01%	0.01%	
N	1.68%	1.78%	
S	0.40%	0.43%	
time (from the beginning, min.)	72	132	176
FB material	Sand		
in raw dry gas	mg/m ³	mg/m ³	mg/m ³
HCl	4	8	14
HF	3	3	3
H ₂ S	620	570	330
COS	32	51	29
CS ₂	1	0	1
Thiophene	19	10	13
BTX	3110	1660	1200
Total tar - BTX	1189	337	100
Conversion from fuel into gas			
Cl	4 %	10 %	16 %
F	6 %	7 %	7 %
S	39 %	38 %	22 %

Table IX: Comparison of emissions of HCl, HF, sulfur compounds, BTX and heavier tar compounds concentrations in FB gasification of German (sub-bituminous) coal on sand

German coal		
Content of elements	raw (mass %)	dry (mass %)
Cl	0.04	0.04
F	0.004	0.005
N	0.71	0.80
S	0.30	0.34
time (from the beginning, min)	49	67
FB Material	Sand	
in raw dry gas	mg/m ³	mg/m ³
HCl	5	3
HF	2	1
H ₂ S	383	298
COS	94	26
Thiophene	36	27
BTX	2310	1340
Total tar - BTX	152	118
Conversion into gas		
Cl	5 %	3 %
F	14 %	4 %
S	66 %	52 %

3.2 Comparison of HCl, HF and sulfur compounds concentrations in gasification of wood in FB of sand

The conditions of FB gasification of wood on sand particles were: temperature 850 °C, ER \approx 0.25, H₂O/C molar ratio \approx 1.22. The contents of Cl, F, S in wood together with concentrations of HCl, HF, H₂S, COS, thiophene and relevant conversions from fuel to produced gas are summarized for two times in **Table X**. While the time trends of HCl and HF exert weak decrease the H₂S concentration clearly shows significant decrease with increasing time. On the other hand, thiophene concentration in producer gas seems to be rather constant, independent on experimental time. The conversions wood-Cl and wood-F into gaseous HCl and HF in fuelgas was higher than for gasification of coals, but also contents of chlorine and fluorine in wood were lower than in the coals used. Nevertheless, the concentrations of HCl and HF in fuel gas from wood FB gasification are significantly higher than in the fuel gas from German coal gasification. This finding is probably coupled with several times higher content of reactive alkali+ alkali earth metals in German coal in comparison with wood.

The overall length of wood gasification on sand particles was about 360 min. The balance of fuel carbon and hydrogen balance (from fuel H and input H₂O) is in **Table XI**. As can be seen, the accumulation of carbon in FB during gasification was lower than in the case of German coal, but still important.

Effect of experimentation time on tar yield and speciation of tar compounds in gasification of wood in FB of sand particles is illustrated in **Fig. 5**.

Table X: Hard wood FB gasification on sand particles – emissions and conversions

Hard wood		
Content of elements	raw (mass %)	dry (mass %)
Cl	0.01	0.01
F	0.003	0.003
N	0.17	0.19
S	0.02	0.02
time (from the beginning, minutes)	105	254
FB material	Sand	
in raw dry gas	mg/m³	
HCl	19	18
HF	4	3
H ₂ S	34	15
COS	4	2
Thiophene	7	7
BTX	16050	14680
Total tar - BTX	9320	7830
Conversion into gas		
Cl	36 %	34 %
F	30 %	23 %
S	51 %	23 %

Table XI: Mass balance of fuel carbon and hydrogen overall balance for wood gasification in FB of sand particles

Elemental balance	
(mol/h)	First part of the experiment (Sand in the FB)
C fuel input	52
C gas output	44
Difference (FB accumulation)	8
Which corresponds to	16 %
H fuel and H ₂ O input	203
H dry gas output	59
H difference (output in H ₂ O)	144

- type V - heavy polyaromatic compounds (4 and more rings)
- type IV - light polyaromatic compounds (2-3 rings)
- type III - aromatic compounds (single ring)
- type II - heterocyclic compounds

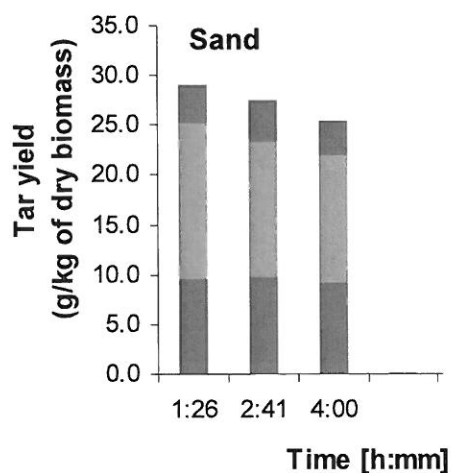


Fig. 5: Effect of time of gasification experiment on tar yield and tar compounds speciation for FB gasification of hard wood on quartz sand

The time trends of tar yield for gasification on sand particles (**Fig. 5**) can be explained by accumulation of mainly wood-char particles and some alkalis in FB.

3.3 Comparison of HCl, HF and S-compounds emissions in gasification of German coal in FB of sand and sand + dolomite particles

The concentrations of HCl, HF, sulfur compounds, BTX and heavier tar compounds in dry fuel gas from FB gasification of German coal on sand particles with bath additions of dolomite particles are shown in **Table XII**.

The concentrations of impurities are lower in presence of dolomite particles and dust in comparison with only sand particle FB gasification (**Table IX**). There are in principle two reasons for this finding: effect of CaO from calcined dolomite on more efficient binding of HCl, HF and H₂S and partly also diluting effect of steam reforming reactions (catalyzed by CaO) of CH₄, C₂H₄, BTX and tar compounds leading to higher gas yield and therefore reduction of concentrations of all present emission components in producer gas.

In presence of dolomite, particularly COS and thiophene concentrations drop substantially during time of gasification. On the other hand, time trend in HCl and HF emissions in presence of dolomite is not quite clear – either constant or moderate increase of concentrations have been observed. The conversions of coal-Cl and coal-F into gaseous HCl and HF are comparable for gasification of German coal on sand and sand + dolomite particles.

The conversions of Cl and F from the coal to gaseous compounds (HCl and HF are very low, but on the other hand, the sulfur conversion from coal to S-compounds in gas are high over 50 % for sand FB and over 30 % for dolomite regular additions.

The effect of dolomite on tar yield in FB gasification of German (reactive) coal is obvious mainly for heavier tar compounds (total tar – BTX) concentrations. The effect of dolomite addition to the sand bed was substantially lower than corresponding effects in wood gasification. The main reasons are: relatively higher concentrations of reactive char in FB and simultaneously some content of reactive CaO (from the ash) in coal-char in comparison with wood gasification.

Despite of substantial decrease of heavier tar compounds concentrations (sum of naphthalene and higher PAH concentrations about 14 mg/m³) in long term gasification with accumulation of char in the FB, the estimated dew point of tar compounds in dry gas is still ^ 29 about 35 °C, which value is rather near at the maximum for long term application of the fuel gas in internal combustion (IC) gas engines.

The sulfur compounds concentrations over 200 mg/m³ are also “at the edge of acceptability” from the point of view of emissions and engine corrosion. For other applications of producer gas (gas turbine, catalytic processes for production of liquid fuels and chemicals) the concentrations of sulfur compounds, HCl and HF are unacceptable. It means that downstream the gasifier gas cleaning method have to be applied.

Table XII: Comparison of emissions of HCl, HF, sulfur compounds, BTX and tar concentrations in FB gasification of German coal sand + dolomite particles

German coal		
Content of elements	raw (mass %)	dry (mass %)
Cl	0.04	0.04
F	0.004	0.005
N	0.71	0.80
S	0.30	0.34
time (from the beginning, min)	58	302
FB Material	Sand + dolomite	
in raw dry gas	mg/m ³	mg/m ³
HCl	1	3
HF	1	1
H ₂ S	239	205
COS	70	19
Thiophene	19	3
BTX	1970	760
Total tar - BTX	82	14
Conversion into gas		
Cl	1 %	3 %
F	7 %	9 %
S	45 %	35 %

4. Conclusions

Coal char accumulation in FB gasification causes particularly in the case of reactive (German) coal decrease of tar compounds concentrations. Combined effects of coal char with

special ash composition (higher Ca and Fe content) have beneficial effect on HCl, HF and on S-compounds emissions (particularly thiophene).

The less reactive bituminous coals (SA-coal) with high content of SiO₂ and Al₂O₃ in ash can exert elevation of HCl emission during time of gasification with accumulation of coal char in bed. The main reason is probably reaction of primarily formed CaCl₂ with SiO₂ leading to formation of calcium silicates and volatilization of HCl. The S-compounds concentrations in producer gas, however, always decrease during time of FB gasification.

Presence of calcined dolomite together with sand in FB gasification has prevailing positive effect on reduction of emissions of HCl, HF, sulfur compounds and tar for reactive coals (German coal). Even emissions of organic sulfur compounds (thiophene and benzo-thiophene) are reduced. In comparison with batch FB of dolomite calcine particles the mixtures of sand with dolomite calcine and compensation of attrited dolomite by regular addition of fresh dolomite has enhanced beneficial effects, mainly on fixed carbon conversion/reduced C-accumulation, tar destruction and sulfur-compounds emissions.

Heavier tar compounds concentrations in fuel gas from FB gasification of reactive subbituminous coal (German coal) are lower than corresponding tar compounds concentrations in FB gasification of wood or less reactive bituminous (SA) coal. Accumulation of coal-char in FB significantly reduces tar compounds concentration in producer gas from reactive coal gasification.

Emissions in FB gasification of wood on sand particles can be reduced by presence of calcined dolomite particles (dust). Particularly the tar emissions can be several times lower.

The in-bed measures (accumulation of char/ash, addition of dolomite) for abatement of HCl, HF and sulfur compounds concentrations lead to fuel gas purity, which is practically at the border of acceptability for IC gas engines. The resulting gas purity is still insufficient from the point of view of requirements of catalytic processes for production of liquid fuels and fuel cells (SOFC) applications. Therefore, downstream deep cleaning methods for fuel gas have to be applied.

Acknowledgements

The authors appreciate financial support from EU Research Fund for Coal and Steel, grant RFCR-CT-2010-00009, support of Technological grant agency TACR (project BROZEN, No. TA01020366) and partial support from the Ministry of Education, Youth and Sport of Czech Republic (specific university research, No. 21/2012).

References

1. Hofbauer H., Rauch R., Ripfel-Nitsche K.: Report on Gas Cleaning for Synthesis Applications Work Package 2E: "Gas treatment", Vienna, University of Technology, Institute of Chemical Engineering, October 2007.
2. Pinto F., Lopez H., Andre R.N., Gulyurtlu I., Cabrita I: Effect of catalysts in the quality of syngas and by-products obtained by co-gasification of coal and wastes. 2: Heavy metals, sulphur and halogen compounds abatement, *Fuel* **87**, 1050–1062 (2008).
3. Cheah S., Carpenter D.L., Magrini-Bair K.A.: Review of Mid- to High-Temperature Sulfur Sorbents for Desulfurization of Biomass- and Coal-derived Syngas, *Energy & Fuels*, **23**, 5291–5307 (2009).
4. Zwart R.W.E.: Gas cleaning downstream biomass gasification Status Report 2009, ECN (The Netherlands), report ECN-E-08-078, June 2009.
5. Cui H., Turn S.Q., Keffer V., Evans D., Tran T., Foley M.: Contaminant Estimates and

- Removal in Product Gas from Biomass Steam Gasification, *Energy & Fuels* **24**, 1222–1233 (2010).
6. Corella J., Toledo J.M., Molina G.: Performance of CaO and MgO for the hot gas clean-up in gasification of a chlorine-containing (RDF) feedstock, *Bioresource Technol.* **99**, 7539-7544 (2008).
 7. Yrjas P., Iisa K., Hupa M.: Limestone and dolomite as sulfur absorbents under pressurized gasification conditions, *Fuel* **75**, 89–95 (1996).
 8. Partanen J., Backman P., Backman R., Hupa M.: Absorption of HCl by limestone in hot flue gases. Part I: the effects of temperature, gas atmosphere and absorbent quality, *Fuel* **84**, 1664–1673 (2005).
 9. Hartman M., Trnka O., Svoboda K.: Potential of calcium oxide for removal of hydrogen sulphide and carbonyl sulphide from coal gas. (Eng) *Acta Montana Ser. B* **112**(9), 5-18 (1999).
 10. Pinto F., Lopez H., Andre R.N., Dias M., Gulyurtlu I., Cabrita I: Effect of Experimental Conditions on Gas Quality and Solids Produced by Sewage Sludge Cogasification. 1. Sewage Sludge Mixed with Coal. *Energy & Fuels*, **21**, 2737-2745 (2007).
 11. Wei X., Schnell U., Hein K.R.G.: Behaviour of gaseous chlorine and alkali metals during biomass thermal utilization, *Fuel* **84**, 841-848 (2005).
 12. Babich I.V., Moulijn J.A.: Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, *Fuel* **82**, 607–631 (2003).
 13. Park N., Lee J.D., Lee T.J., Ryu S.O., Chang C.H.: The preparation of a high surface area metal oxide prepared by a matrix-assisted method for hot gas desulphurization *Fuel* **84**, 2165-2171 (2005).
 14. Dhage P.P.: Promoted ZnO Sorbents for Wide Temperature Range H₂S/COS Removal for Applications in Fuel Cells, Ph.D. Thesis, Graduate Faculty of Auburn University Auburn, Alabama, USA (2011).
 15. Hidetoshi Kuramochi H., Wu W., Kawamoto K.: Prediction of the behaviors of H₂S and HCl during gasification of selected residual biomass fuels by equilibrium calculation, *Fuel* **84**, 377–387 (2005).
 16. Stahlberg P., Lappi M., Kurkela E., Simell P., Oesch P., Nieminen M.: Sampling of contaminants from product gases of biomass gasifiers, Research notes 1903, Technical Resear Centre of Finland, Espoo (1998).
 17. Skácel F., Tekáč V.: Podklady pro MŽP ČR k provádění protokolu o PRTR – přehled metod měření a identifikace látek sledovaných podle Protokolu o registrech úniku a přenosů znečišťujících látek do ovzduší, Stanovení fluoru a anorganických sloučenin jako HF, VŠCHT Praha (2007).
 18. Hepola J.: Sulfur transformations in catalytic hot-gas cleaning of gasification gas, VTT publication No. 425, VTT Technical Research Center of Finland, Espoo 2000.
 19. Magel F.P.: Electricity from wood through the combination of gasification and solid oxide fuel cells Systems analysis and Proof-of-concept, Ph.D. thesis, ETH Zurich, Switzerland (2008).
 20. Pohořelý M., Vosecký M., Hejdová P., Punčochář M., Skoblia S., Staf M., Vošta J., Koutský B., Svoboda K.: Gasification of Coal and PET in Fluidized Bed Reactor, *Fuel* **85**, 2458–2468 (2006).
 21. Pohořelý M., Svoboda K., Hartman M.: Feeding Small Quantities of Particulate Solids. (Eng). *Powder Technol.* **142**(1), 1-6 (2004).
 22. The international standard for tar and particle measurement in biomass producer gas, available from: <http://www.tarweb.net>
 23. Czech Norm Institute: ČSN P CEN/TS 15439. Zplyňování biomasy – Dehet a částice v plynných produktech – Vzorkování a analýzy, Český normalizační institut (2006).

24. EN 1911-1: 1999 zavedena v ČSN 1911-1 Stacionární zdroje emisí – Manuální metoda stanovení HCl – Část 1: Vzorkování (ČSN 83 4750-1). Czech Norms: Manual method for determination of HCl –part 1: sampling.
25. EN 1911-2: 1998 zavedena v ČSN 1911-2 Stacionární zdroje emisí – Manuální metoda stanovení HCl – Část 2: Absorpce plyných složek (ČSN 83 4750-2), in Czech Norms: Manual method for determination of HCl-part 2: absorption of gaseous components.
26. EN 1911-3: 1999 zavedena v ČSN 1911-3: Stacionární zdroje emisí – Manuální metoda stanovení HCl – část 3: Analýza absorpčního roztoku a výpočty (ČSN 834750-3).
27. EN 83 4752:1989 zavedena v ČSN 83 4752: Ochrana ovzduší – Stanovení emisí fluoru ze stacionárních zdrojů (83 4752). ČSN 834752-1-5: Stanovení emisí fluoru ze stacionárních zdrojů, část 1-5 odběr a metody stanovení, ČSNI Praha (1990).
28. Partanen J.: Chemistry of HCl and Limestone in Fluidised Bed Combustion, Report 04-1, Fac. of Chem. Engineering, Abo Academi, Finland (2004).
29. Estimation of tar dew point from tar components concentration in producer gas:
www.thersites.nl