

# Online water vapor detection in the product gas from indirect gasification

(Onlinebestämning av vattenånga i produktgasen från  
indirekt förgasning)

Sergey Cherednichenko, Hosein Bidgoli, Jens Nordmark, Martin Seemann

*"Catalyzing energygas development  
for sustainable solutions"*

**ONLINE WATER VAPOR DETECTION IN THE PRODUCT GAS FROM INDIRECT GASIFICATION (ONLINEBESTÄMNING AV VATTENÅNGA I PRODUKTGASEN FRÅN INDIREKT FÖRGASNING)**

Sergey Cherednichenko, Hosein Bidgoli, Jens Nordmark, Martin Seemann

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Malmö, Sweden 2013

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## Foreword

The project has been a collaboration between the Dept. of Microtechnology and Nanoscience and Department of Energy and Environment, Chalmers University of Technology.

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## Summary

The integration of a gasifier into a complex synthesis process, such like SNG synthesis, with several process steps asks for a better monitoring of the gasifier performance. While the dry gas composition is often known, tar concentration and steam concentration in the raw producer gas are usually not available online. A set of standard analyzers for dry gas composition (GC or NDIR) and online tar measurement combined with an online water measurement could allow the continuous calculation of simple mass and energy balances. Those balances, that characterize the gasification process, could enable the operator to monitor the effects of varying fuel properties and eventually counter the effects on the downstream equipment.

For the detection of steam concentration in raw gas electromagnetic waves of terahertz frequencies (hundreds of gigahertz) are promising with regard to develop a robust online measurement device for industrial application. Main reasons for the high potential are the low risk for interference with the wide range of other molecules and the fact that THz frequencies are rather insensitive to deposits and particulate matter in the course of the beam, compared to laser technology at IR. Aiming to test the feasibility of applying this measurement technique in the industrial scale, a gas cell was designed and constructed providing conditions close to the onsite operation (i.e. T, P, gas composition, etc.) for primary laboratory tests. The experiments were then followed with onsite tests at Chalmers power central. Within those experiments the application of THz spectroscopy as a promising technique for detection and measurement of steam and CO at real industrial processes was proven. Current report demonstrates the procedure of implementing a THz spectrometer to acquire data in both laboratory and industrial scale and discuss how those data could be interpreted to gain a precise measurement of desired gaseous components.



## Sammanfattning på svenska

Mätmetodik inom området förbränning och förgasning i storskaliga processanläggningar är idag baserad på tekniker där man antingen suger ut gas med en sond och därefter bereder gasen innan den skickas in i olika mätutrustningar, t.ex. gaskromatograf, eller olika typer av joniseringstekniker, alternativt sätter man in olika sensorer som mäter förhållandena vid sin spets, t.ex. termoelement och lambdasensorer. Utsugsmetoderna är mycket noggranna, men skapar alltid en osäkerhet kring hur själva provtagningen och beredningen påverkar mätresultatet. För dessa metoder har man alltid en tidsfördröjning och får ett volym-tidsmedelvärde. Dessutom påverkas många av de intressanta komponenterna av beredningsprocessen. När man använder sensorer kommer man runt vissa av dessa nackdelar, men för dessa skapas andra osäkerheter i och med att man stoppar in en fysisk kropp i den punkt man vill mäta en parameter. Den lokala strömningsbildningen påverkas och andra faktorer som t.ex. strålning gör att mätningen inte blir så lokal som man önskar. Sammanfattningsvis, de mätmetodiker som tillämpas idag har begränsade möjligheter att studera transienta och lokala förlopp, vilket begränsar möjligheten att öka förståelsen om vad som verkligen händer i storskaliga förbrännings- och förgasningsutrustningar och därmed gör att det finns en stark önskan inom forskningsområdet att introducera nya mätmetoder som inte har dessa begränsningar.

Tekniker som har de egenskaper som efterfrågas har under de senaste årtionden utvecklats och har hittat applikationer inom främst motor- och gasturbinindustrin, men för de förhållanden som råder i en förgasare eller i olika eldstäder har dock teknikerna ännu inte slagit igenom. Detta faktum gör att det idag inte finns kommersiella analysatorer att köpa och ingen metodik framtagen för dess användning i dessa tillämpningar med undantag för några få specifika specialområden. Gemensamt för dessa tekniker är att man gör mätningarna genom att mäta olika spektra där man sänder ut ljus eller mikrovågor i olika frekvenser och sedan mäter hur dessa spektra förändras, vilket är en funktion av sammansättning, temperatur och tryck. I en förbrännings- eller förgasningsanläggning är det inte rakt fram hur man ska använda dessa tekniker då storleken på anläggningarna och begränsad tillgänglighet gör det svårt att placera ut sändare och mottagare på lämpliga platser. Dessutom begränsas möjligheterna av dess användning ofta av höga halter av partiklar, stora temperaturgradienter, vibrationer, och interferenser av olika ämnen inom vissa våglängdsområden. Det gäller därför att välja rätt teknik som klarar extrema koncentrationer av exempelvis koldioxid och vattenånga som är vanliga i vissa applikationer, t.ex. oxyfuel/CLC-förbränning, samt förgasning av biomassa.

Inom Chalmers finns de olika kompetenserna och experimentella utrustningarna som behövs för att utveckla beröringsfria mätmetoder för förbrännings- och förgasningsförhållanden i olika processanläggningar och detta projekt utnyttjar Chalmers samlade kompetens.

I detta projekt undersöktes möjligheten att använda mikrovågor för online-mätningar av vattenånga och kolmonoxid vid hög temperatur (300-800 °C). För detta ändamål byggdes en mobil mätvolym anpassad för sensorerna, där gas från Chalmers pilotförgasare kan tas in utan att kylas, alternativt gas som blandas från gastuber och ånggeneratorer och värms till relevant temperatur. Till den konstrue-



rades en lämplig Thz-gasspektrometer som tillåter evaluering av olika parametrar som *signal to noise ratio* och förväntad noggrannhet. Gasspektrometer och gascellen testades sen vid relevanta processbetingelser på labb med olika gasblandningar. Till sist så kopplades systemet till en sidoström av rågas från Chalmersförgasaren och demonstrerade funktionen med både rökgas och rågas. Ånghalten i rågasen mättes även vid varierande ångkoncentrationer.

Slutsatser från projektet är:

- a) Mätcellen uppfyllde funktionen, dvs. jämn temperatur, bra temperaturhållning, täthet
- b) Olika testade material har visat sig vara genomskinliga för THz-vågor och är därmed tänkbara som fönster i mätcellen. För testerna på Chalmers valdes kvartsglas som kan motstå höga temperaturer och skapar låga förluster i mätvägens intensitet.
- c) Uppmätta resultat för ånga och kolmonoxid motsvarar väl de modellerade spektra
- d) Med mätuppställningen som den är idag är det möjligt att detektera ändringar på procentnivå med en tidsupplösning av en minut
- e) CO-absorptionen kan mätas väldigt väl i torra gasblandningar men med mindre precision med höga ånghalter
- f) THz-spektra av vattenånga och CO påverkades inte av andra komponenter i rågasen
- g) En uppgraderad version av mätuppställningen (framförallt en uppgradering av THz-detektorn) kommer att minska tidsupplösningen och öka robustheten samt minska den fysiska dimensionen
- h) Data av hög kvalité saknas för att modellera gasspektra i temperaturområde kring 800 °C. Det krävs dedikerade labbförsök för att komplettera databasen.
- i) Tester över 400 °C är mycket intressant för framtida arbeten

Projektet har skapat underlag för utveckling av online-metoder för gasanalys nedströms av en förgasningsanläggning. Mätningar kommer kunna användas i både optimering och styrning av processen med tanke på en avancerad syntesprocess nedströms förgasaren.



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## 1. Background

### 1.1. Measurement of H<sub>2</sub>O content in raw gas

Biomethane or SNG is one of the most promising alternatives of 2<sup>nd</sup> generation biofuels. Sweden as a country with abundant natural resources in form of forests products and agricultural residues has the capacity to demonstrate a remarkable contribution between the transportation sector and biofuel production industry. This contribution would definitely be inevitable if Sweden wants to achieve a fossil-free transportation sector by 2030.

However, the major obstacle toward reaching this goal is that most of the biomass resources are sought-after by other sectors too, and hence they should be used in the most efficient way. To avoid conflicts with other industries like pulp and paper industry or food production the most interesting feedstock for synthetic fuel production are low grade ones such as bark, "grot" or agricultural wastes. Thus, due to the limited resource, gasification technology has to be efficient and fuel flexible (low grade fuels).

As the gasification in an SNG synthesis plant is an integrated part in a complex system, variations in the product gas must be avoided or detected early to adjust downstream equipment or to protect catalysts. Ideally, the operation of the gasifier can be adjusted continuously to meet the downstream requirements despite variation of the fuel quality. Basis for a continuously process adjustment are simple energy and mass balances based on robust measurement techniques. However, the characterization of raw gas from biomass gasification is a troublesome undertaking. With the state of the art measurement technology the gas is cooled, condensate is separated from the permanent gases and all phases are analyzed separately.

While the gas composition (permanent gases) can be measured continuously after a scrubbing device, tar concentrations and water content are available with large time delays. For tars the first steps are done to develop an online analysis based on laser-induced fluorescence. Nevertheless, such development is missing for the water concentration, which is a vital input to the energy and mass balance. Available IR techniques do not cope fully with the complexity of the gas mixture (interference of bands), the presence of particulates in the gas and the risk for dirt layers on the windows. A solution could be the detection of water at terahertz frequencies ((1THz=10<sup>12</sup> Hz)) which is a proven technology in other applications and a promising way to get around the aforementioned problems of IR-spectroscopy. As detection at THz frequencies can potentially provide information about both steam concentration and carbon monoxide (CO) as a representative of the "permanent" gas compounds, the values can be combined easily with the results from standard analyzers for H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>x</sub>, C<sub>3</sub>H<sub>x</sub> obtained in a dried gas stream. Due to the fact that those wavelengths penetrate a broad variety of opaque materials the analyzer will be low sensitive to dirt and particulates present in the raw gas. Online tar measurement based on laser induced fluorescence would complement the producer gas measurement. Together with operation parameters, such as fuel feed, temperatures and steam flows, mass and energy balances can then be set up at the rate of the slowest analyzer.



## 1.2. THz spectroscopy: general principle

Electromagnetic (EM) waves experience absorption ( $A$ ) by the media the waves propagate through. The ratio of the incident EM power to the output EM power is called transmission coefficient ( $T=1-A$ ). Transmission coefficient decreases with the optical propagation path according to the Beer law:  $T(x)=\exp(-x\alpha)$ , where  $\alpha$  is the absorption coefficient (characteristic to the material and the frequency of the EM wave).

An EM wave could strongly be absorbed when propagating through a gas if the frequency of radiation corresponds to the molecular transition energy (frequency) of a certain degree of freedom. For EM waves at THz range, absorption occurs on the rotational degrees of freedom of a molecular gas. Due to the molecular chaotic movement, as well as collisions between molecules, the absorption frequency broadens to an absorption line with a width proportional to the gas pressure and temperature. On the gas transmission spectrum, ( $T(f)$ ), absorption lines appear as minima at different frequencies. The absorption intensity (i.e. depth of the minima) is generally a function of the optical path length, the absorbing gas concentration, and finally, the gas temperature. At large gas concentrations and very high absorption intensity, even the transmission between the absorption lines (continuum absorption) could be affected by the lines to some extent (see Figure 1 for illustration).

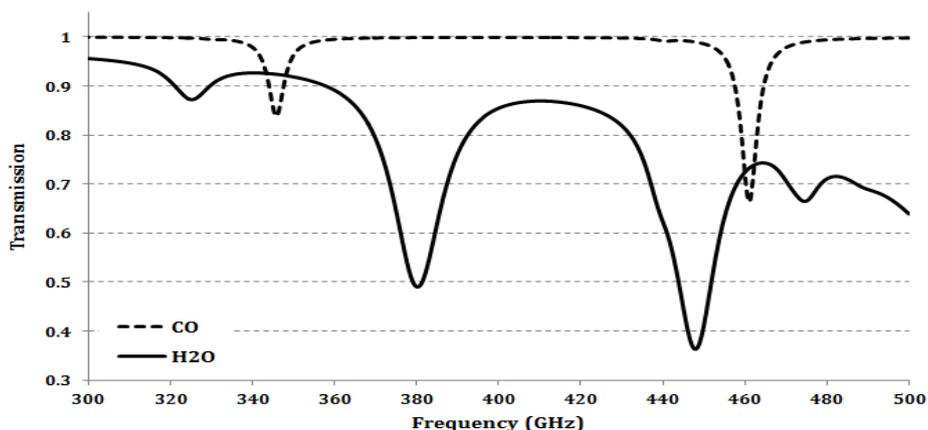


Figure 1: Simulated transmission profiles for  $N_2$ - $H_2O$  gas mixture with  $VMR_{H_2O}$ : 0.2 (solid line) and  $N_2$ - $CO$  mixture with  $VMR_{CO}$ : 0.2 (dashed-line) at normal condition (Rothman et al., 2009).

The THz region lies between the microwave and infrared regions of the electromagnetic spectrum and covers the frequency range between 0.1-10 THz. Energy transitions between rotational degrees of freedom of small gas molecules like  $H_2O$  and  $CO$  are of the order of a few meV corresponding to the photon energy of electromagnetic waves at this frequency range.

Detection and measurement of the concentration of such gases based on gas-spectroscopy principles is thus feasible in theory. To do so, the location and strength of line centers corresponding to gaseous form of  $H_2O$  as well as  $CO$  at the frequency range between 300-500 GHz should firstly be identified and trans-



mission spectra have to be simulated at various conditions using gas line databases such as HITRAN and GEISA (Rothman et al., 2009).

According to the databases pure rotational water lines at 448 GHz and 380 GHz show a promising potential to be applied as the reliable indicators for acquiring water concentration in complex gaseous mixtures at temperature range up to 800 °C (Figure 1). Although much weaker compared to the mentioned water lines, CO lines at 345 and 460 GHz also have possibility to be used in quantifying the concentration of this gas in mixtures.



## 2. Experimental

### 2.1. Construction of the THz gas spectrometer

A gas-spectrometer was designed and constructed to fulfill the general requirements of gas spectroscopy of gaseous H<sub>2</sub>O at THz frequencies and withstand the harsh condition in the hot gas streams coming out from the Chalmers gasifier. The setup comprised a gas-cell made of stainless steel with a length of 1.6 m and an inner diameter of 3.4 cm (Figure 2).

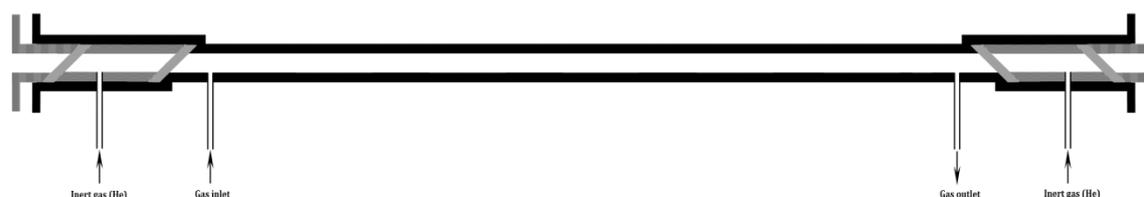


Figure2: Schematic view of the gas-cell.

The gas-cell was designed to provide a layer of hot gas with the thickness of 1 m continuously flowing through a straight hot duct and being exposed to radiation through two layers of windows. The 1 m propagation in the gas with the anticipated H<sub>2</sub>O and CO concentrations shall provide absorption at the resonant frequencies strong enough to be detected by the system described below.

The inner and outer windows in each side of the hot duct were made of 4 mm thick crystalline quartz and 2 mm thick Teflon (PTFE) sheets, respectively. Quartz is capable to withstand heating to above 1000 °C. It is also known to have a rather low absorption for EM waves of the THz range. The windows had the inclination of 60° (close to the Brewster angle) relative to the radiation pathway to minimize the reflections occurring at the window surfaces for the EM wave polarized parallel to the incidence plane. Teflon is also known for a low damping of the THz waves, and it is very easy to machine to a design shape.

Volumes between two windows in each side of the hot duct were continuously flushed with a non-absorbing gas such as He or N<sub>2</sub>. The gas-cell was surrounded by a T-controlled heating oven, which keeps the temperature of the walls sufficiently high to prevent condensation of tar and water (Figure 3).

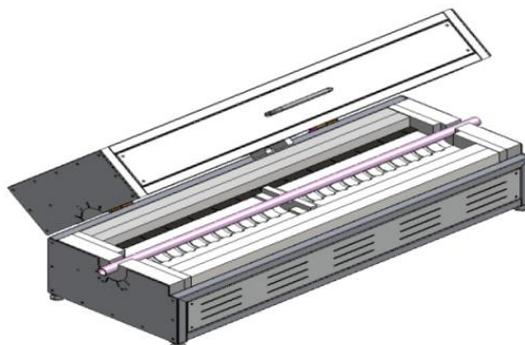


Figure 3: The Gas-cell was encompassed by a T-controlled heating oven.



Formation of temperature gradient along the hot duct was avoided through utilization of two separate heating zones placed in series. The gas temperature was measured by two thermocouples (type K) placed at the inlet and outlet of the duct, thereby it was confirmed that the gas temperature was constant along the hot duct (Figure 4).

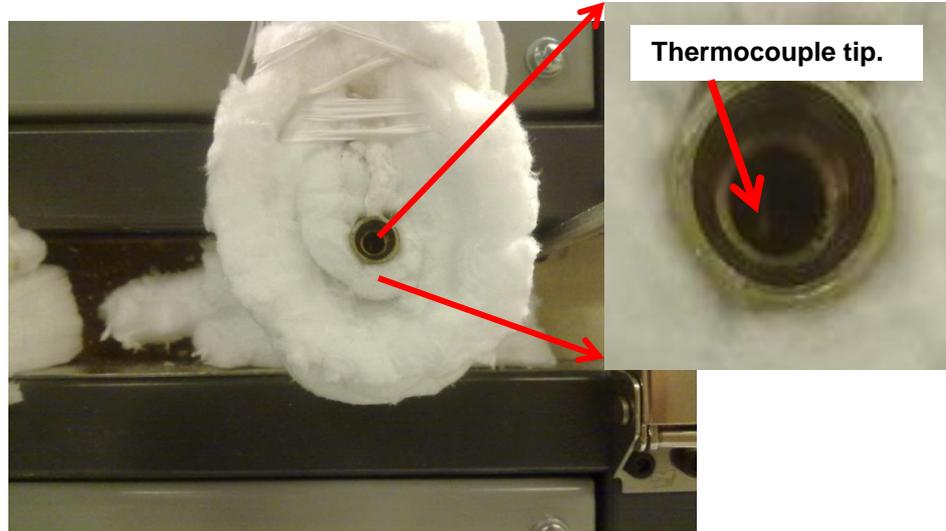


Figure 4: Gas output flange. A thermocouple was inserted to the middle of the tube through a T-connection. The output flange, the T-connection, and the first section of the thermocouple are isolated.

A 300-500 GHz compact THz transmitter with an output power 50-100  $\mu$ W launched the EM waves into the gas cell. A cross-section of the gas-cell much larger than the wavelength facilitates a low loss propagation through a rather long (1.8 m total length) and a low electrical conductivity (stainless steel) duct. A detector with a beam collimator was installed at the opposite side of the gas cell.

To counter the effect of variations in the source amplitude during a long operation time, a part of the beam was split before it went into the cell and sent to a reference detector.

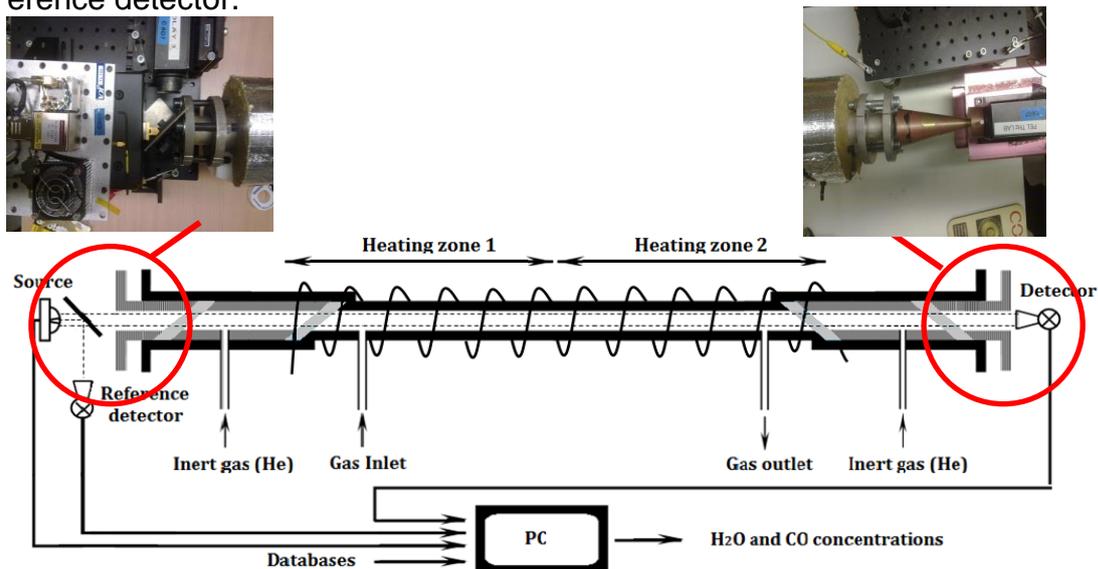


Figure 5: THz gas spectrometer setup.



## 2.2. Instrumentation

The THz transmitter used was a frequency multiplier based Tx-unit (Virginia Diodes Inc. USA, WR 2.2.), which multiplies a microwave signal (8-14GHz) up to the range required in this application (300-500GHz). The frequency of the microwave source was in turn controlled by a DC source integrated in a lock-in amplifier (Stanford Research SR830). The THz wave was amplitude modulated (AM) at 18Hz. To reduce effect of the frequency control voltage instabilities, THz wave was also frequency modulated (FM) at 333Hz (much higher than the AM frequency). The FM was controlled by an AC source in the same lock-in. For detection, a Golyay cell (Tydex, Russia) was used. The detectors outputs were connected to lock-in amplifiers for synchronous detection with a reference signal at the same frequency as for AM modulation of the THz source. Frequency scanning was controlled via GPIB (IEEE 488) interface of the lock-in. The schematic below shows the setup for the instruments.

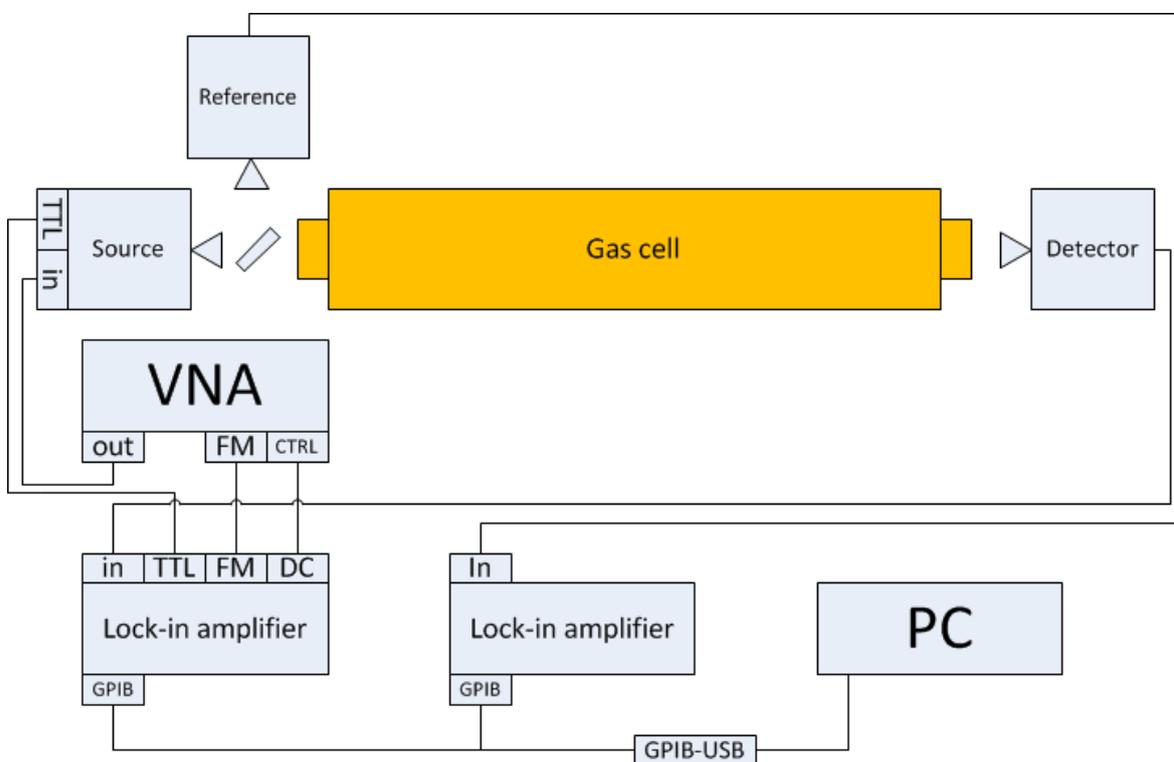


Figure 6: Spectrometer schematic.

## 2.3. Laboratory tests

A part of laboratory tests were performed at the Terahertz and Millimetre Wave Laboratory at the departments of Microtechnology and Nanoscience (MC2) of Chalmers University of Technology. During those experiments a controlled flow of  $N_2$  was preheated and mixed with a flow of water vapor at 105 °C produced by a steam generator. The mixed gas was further heated up to the desirable temperature and introduced to the gas spectrometer. The water content of the gas was evaluated using two separate methods. The first way was based on continuous weighing of water container from which the steam generator was feeding over the



time and calculating the average mass flow of water over that period of time. Although, that measurement method was not time resolved, it could provide a good indication over the absolute average humidity. The second way was measuring H<sub>2</sub>O content through a humidity detector connected to the outlet of gas spectrometer providing relative humidity of the flow with a time resolution of 2 s.

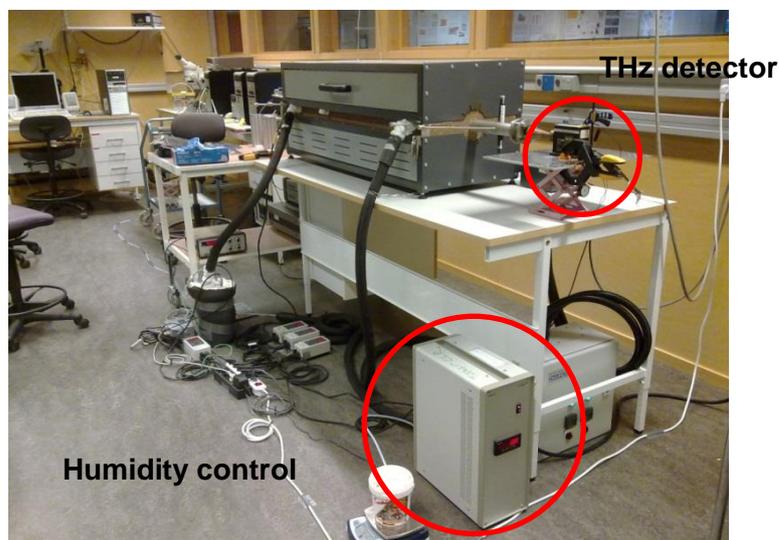


Figure 7: Laboratory setup of the THz gas spectrometer.

The experimental tests with dry CO were conducted at Chalmers power central, where CO bottle was available. At those tests the composition of gas mixture was measured by sending the outflow gas from the THz spectrometer to a Gas Chromatograph (GC) device.

#### 2.4. Onsite tests

During the onsite tests, a split stream of the raw gas from the Chalmers gasifier was connected to the gas spectrometer (Figure 8, 9). The continuous gas flow was held by a pump sucking the raw gas from the gasifier. After passing the THz device, the gas was immediately cooled down (quenched) using cold isopropanol to condensate the tar and water content (scrubbing). The cold dry gas was then sent to GC to measure the permanent gas compositions in an online way with a time delay about 3 min.

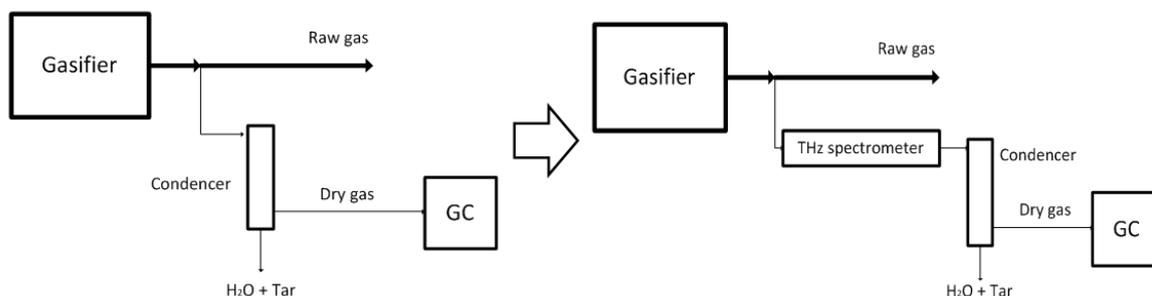
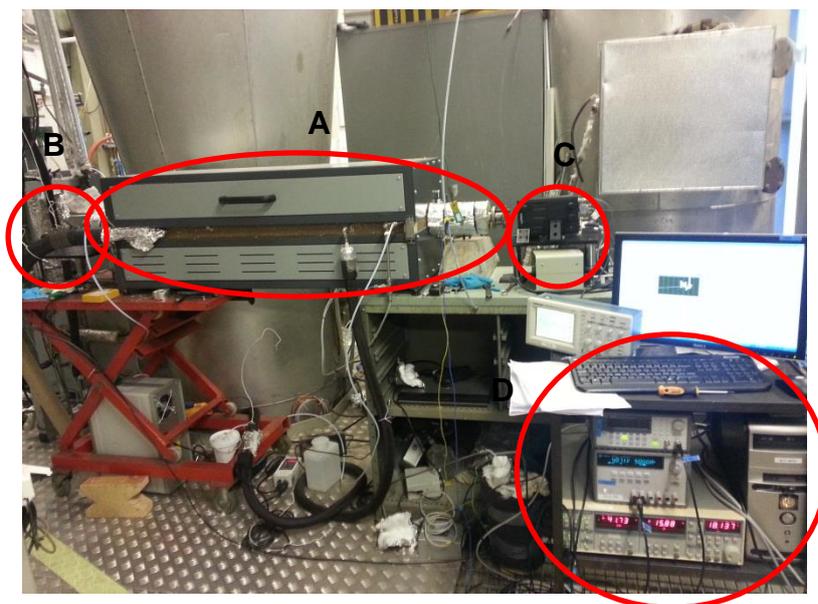


Figure 8: Integration of terahertz spectrometer into the raw gas measurement system.





*Figure 9: Onsite setup of the THz gas spectrometer: A-hot gas cell; B-THz detector, C- THz transmitter; D-control and readout electronics.*



### 3. Results and discussion

#### 3.1. Laboratory tests

Transmission through the gas-cell was measured across the 300 GHz to 500 GHz frequency range. For the spectral calibration a transmission through the same gas-cell filled with nitrogen (non-absorbing gas at the discussed frequencies) was used. Figure 10 illustrates typical full range frequency scans for N<sub>2</sub>-H<sub>2</sub>O mixtures at 350 °C. The water lines at 325, 380, 448, 475 GHz are clearly detectable. However, the lines at 380 and 448 GHz are much stronger and therefore they were used for fitting to the simulation data (smooth curves). By comparing the variation of the transmission at these two frequency lines at different volumetric ratios of H<sub>2</sub>O in the gas mixture it was concluded that the derivative of the transmission versus water concentration is stronger for the 448 GHz line compared to that for 380 GHz (peak absorption at 448 GHz is more sensitive to the water vapor variation than that at 380 GHz). Thus, that line was used to measure the gas transmission for various water vapor concentrations. The transmitter power reduces towards lower and higher ends of the frequency band (to 300 GHz and to 500 GHz). It caused a reduction of the signal to noise ratio at the detector. Due to this reason higher noise can be observed at the lower and the higher ends of the transmission spectra. Oscillations observed between water lines (e.g. between 380 GHz and 448 GHz) are probably caused by the standing waves in the gas cell (remaining reflections from the sealing windows), and those will have to be dealt with during next generations of the instrument.

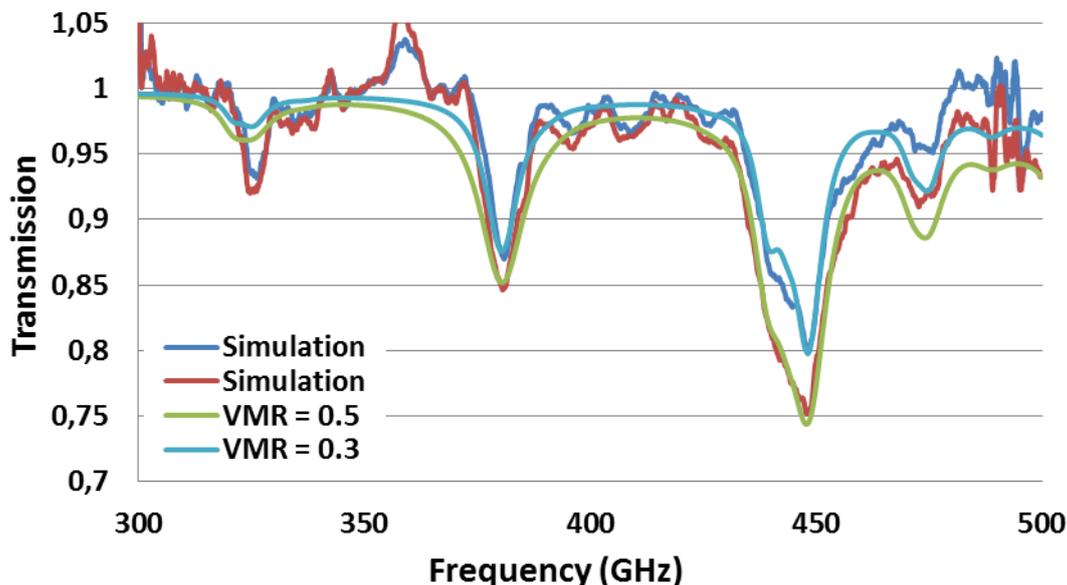


Figure 10: Frequency scans between 300 to 500 GHz for N<sub>2</sub>-H<sub>2</sub>O mixture with two different volumetric ratios of H<sub>2</sub>O (VMR) at 350 °C (Jens, perhaps, insert (as an inset) a non-normalized (raw data) spectra, to show how the transmitted power varies across the frequency band).

Figure 11 shows long time loggings of the THz transmission signal at a constant frequency (448 GHz) for continuous flows of gas mixture (N<sub>2</sub>-H<sub>2</sub>O) with different



water contents. From the figure it can be inferred that the VMR variations as small as 0.5% could be very well resolved using current setup. For instance, the difference between VMR values of 0.155 and 0.159 could be clearly distinguished.

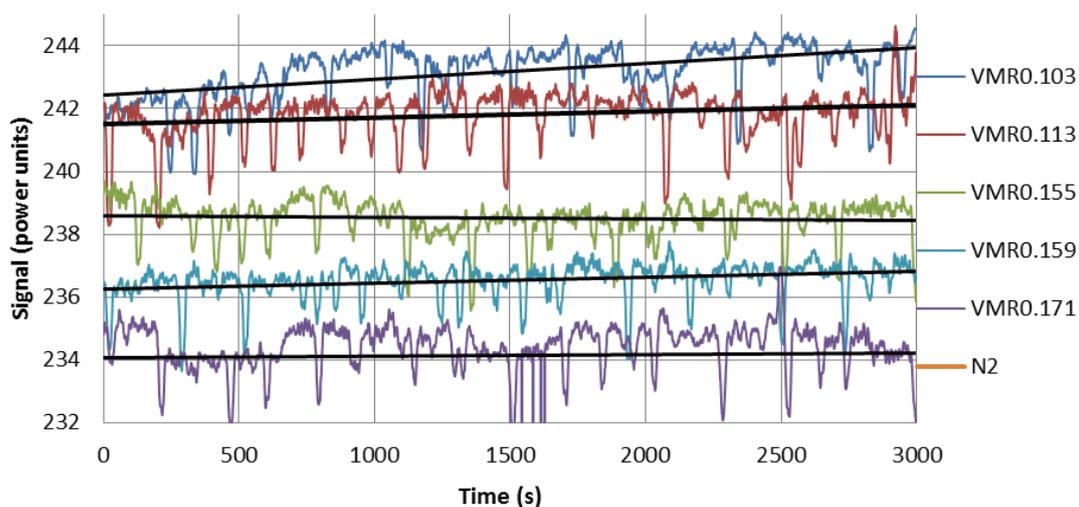


Figure 11: 448 GHz water vapor line (20130204).

The peaks on the curves were later identified to be due to the water vapor pulses, which were also registered by independent measurements of the output gas humidity using humidity detector device and shown in Figure 12 together with a THz signal recorded simultaneously. While looking to the figure, one should note that the signal power has an inverse relation with the humidity level. In other words, with increasing the humidity level (blue line) the signal amplitude (red line) decreases. As shown in the figure, due to the very fast measurement (high time resolution), THz spectrometer can detect very fast oscillations generated by the steam generator. The oscillations were proofed to be originated from steam generator since they could not be seen for pure nitrogen. These steam pulses were later reduced by increasing the flow resistance to the steam flow behind the steam generator.

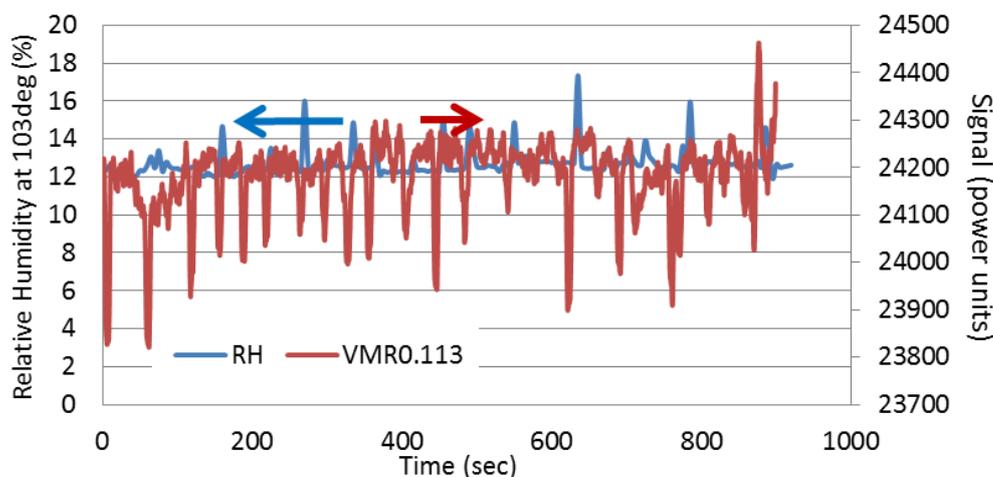


Figure 12: Change in signal amplitude at 448 GHz water vapor line (red line), and relative humidity registered by humidity detector at 103 °C (blue line).



The following tests were conducted at the Chalmers gasifier, however with gas mixtures composed from commercial compressed gas bottles.

The frequency scans between 300 to 500 GHz for a mixture of dry gases i.e. (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, etc.) were performed and the CO lines at 345 and 460 GHz were detected (Figure 13-Figure 15).

Figure 13 demonstrates transmission spectrum of a 22%vol (VMR) CO mixture (red) with a spectrum of pure N<sub>2</sub>. A strong CO absorption is observed at 460 GHz. After normalization of the “CO” spectrum over the “N<sub>2</sub>” spectrum even weaker CO line at 346 GHz can be observed. A smooth line was obtained by simulation for the 22% of the CO mixture. The reason for the line splitting at 346 GHz is not very clear now.

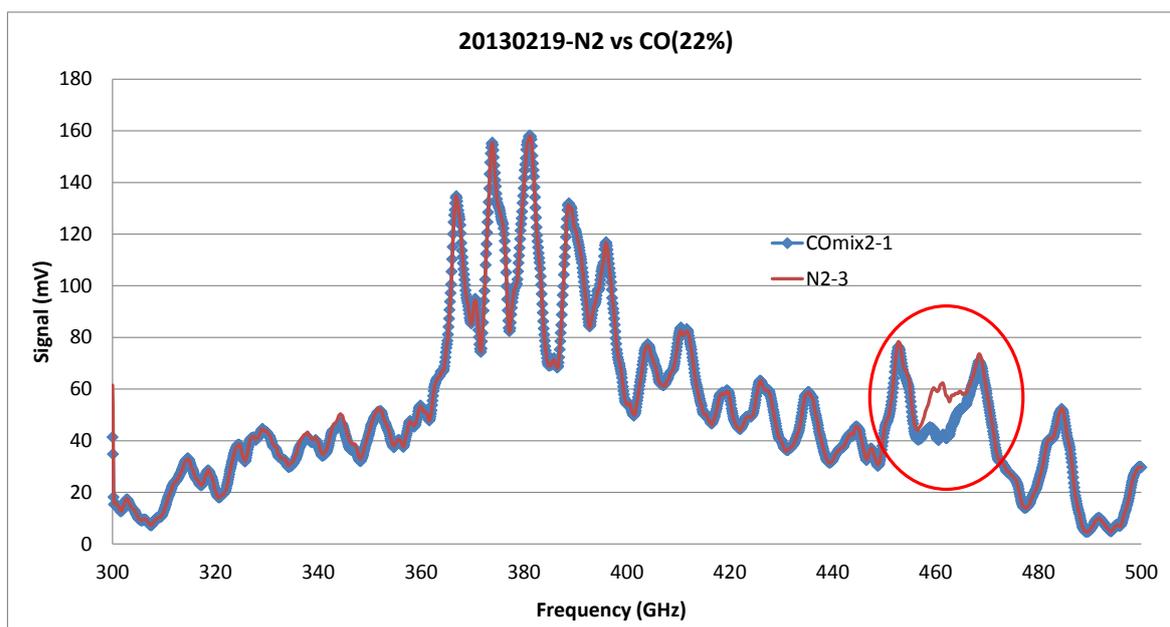


Figure 13: Transmission spectra of a dry (no water vapors) gas mixture containing 22% of CO and of pure nitrogen (N<sub>2</sub>). A strong CO absorption line is seen at 460 GHz. By normalizing the “CO” spectrum on the “N<sub>2</sub>” spectrum, a normalized gas cell transmission spectrum can be obtained (see Figure 14).



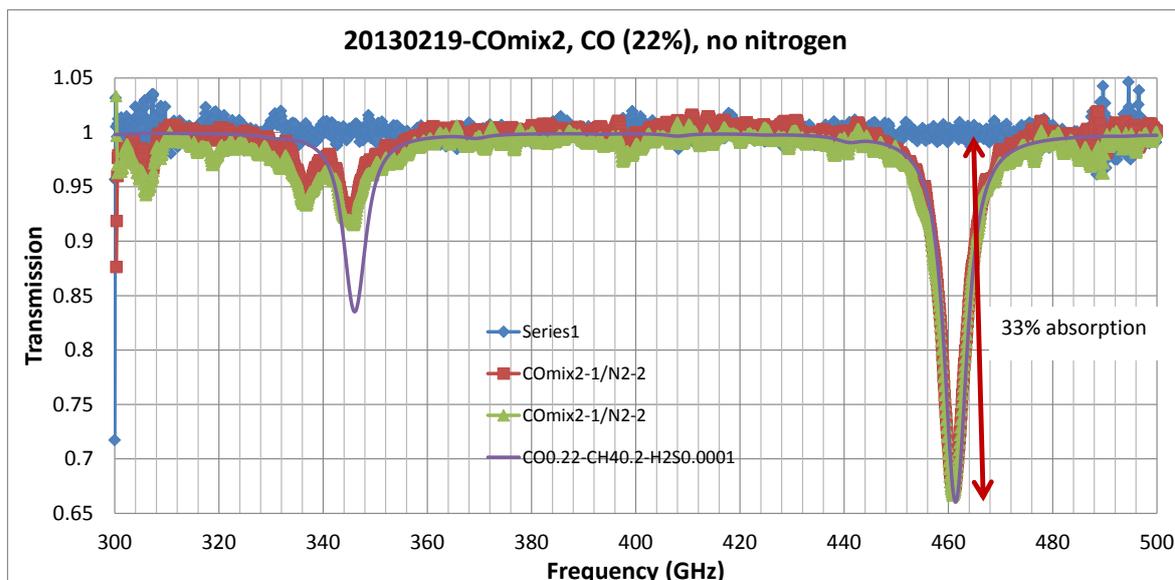


Figure 14: Transmission spectra of a dry (no water vapors) gas mixture containing 22% of CO. versus time at 460 GHz for two levels of CO concentrations. The black lines are representing the same data using 1 minute integration time.

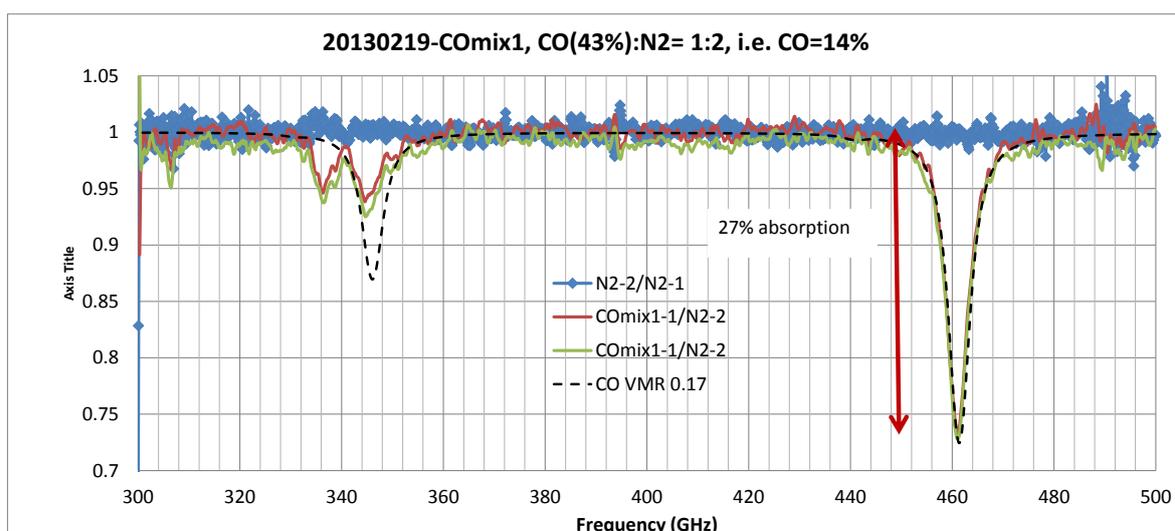


Figure 15: Similar as in Figure 14 for CO mixture of 14%. Simulations fit for a CO VMR of 0.17. The difference might originate from the uncertainties of the gas flow settings.

Online monitoring of the gas cell at 460 GHz (stronger CO line) is presented in Figure 16, where a transition from pure N<sub>2</sub> gas to a 22% mixture of CO is observed.



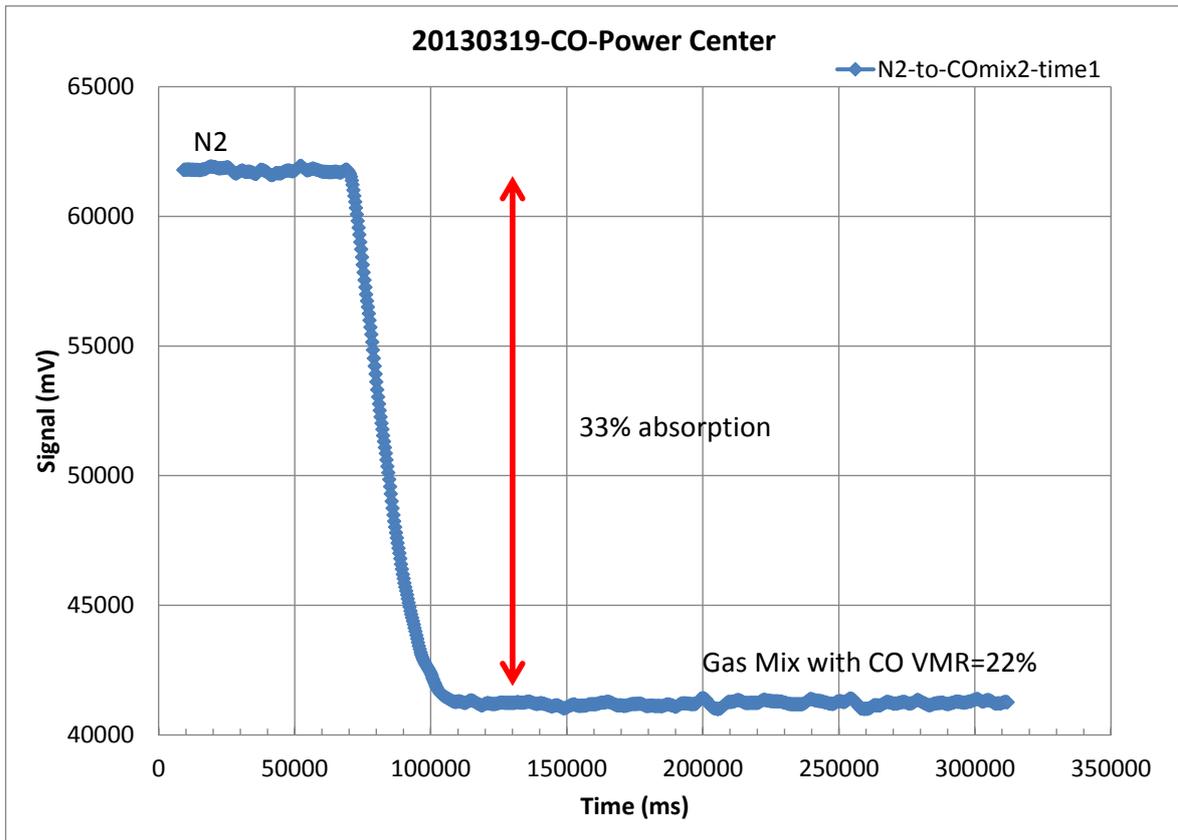


Figure 16: Experimental transmission profiles for raw gas (steam inflow to the gasifier: 180 kg/h) and flue gas along with the best fitted theoretical simulations (dashed- and dotted- lines respectively correspond to VMR values of 0.6 and 0.17 for steam and 0.08 and 0 for CO).

These tests were performed at room temperature in order to exclude the effect of temperature instabilities (from the heated gas cell) on the measurements results. However, we considered the fact that for a given VMR of a gas (e.g. of CO) the absorption intensity reduces at higher temperatures because of the reduction of the molecular concentration (the total pressure is assumed constant).

No laboratory investigation of the CO mixture with water vapor was done because it requires an upgrade of the equipment.



## 3.2. Onsite tests

Full range frequency scans (i.e. 300-500 GHz) were performed for raw gas and flue gas extracted respectively from the gasifier and the boiler. The gas temperature in the gas-cell was 350 °C.

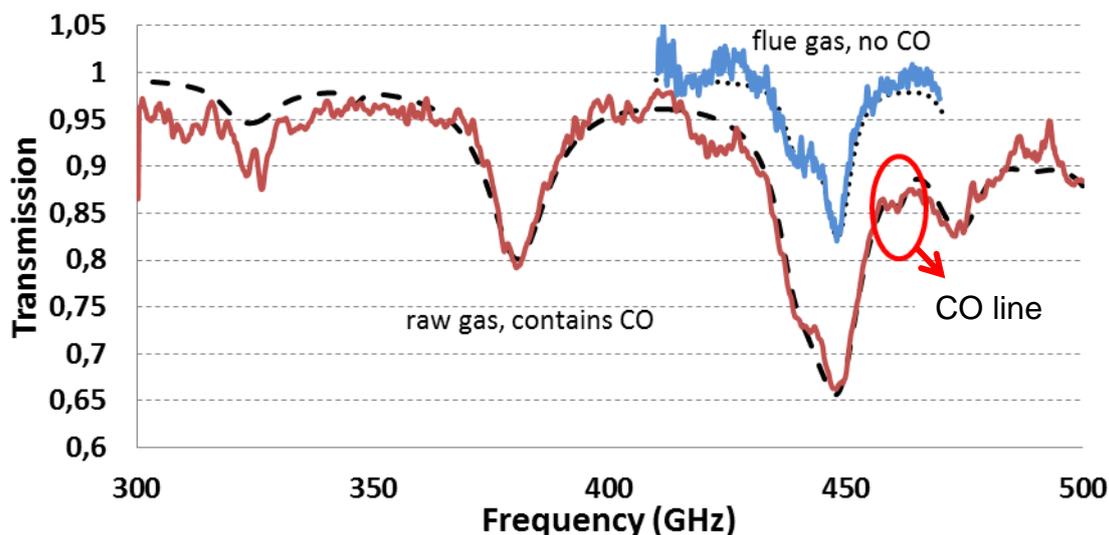


Figure 17: Experimental transmission profiles for raw gas (steam inflow to the gasifier: 180 kg/h) and flue gas along with the best fitted theoretical simulations (dashed- and dotted- lines respectively correspond to VMR values of 0.6 and 0.17 for steam and 0.08 and 0 for CO).

Despite presence of numerous chemical compounds in the raw gas, the full range spectra only showed one unknown line at 420 GHz with no interference to water and CO absorption lines confirming that most of the raw gas components either has no absorption line at the examined frequency range or their VMRs were too low to have notable impact on the transmission spectrum.

The acquired experimental results showed a good reproducibility and were in strong agreement with the simulated spectrum corresponding to a gaseous mixture of  $N_2$ - $H_2O$ - $CO$  ( $VMR_{H_2O}$ : 0.60 and  $VMR_{CO}$ : 0.08) at 350 °C (dashed-line). The location and magnitude of transmission of water lines at 380, 448 and even 475 GHz coincided well with the simulated spectrum. Nonetheless, the observed transmission coefficient at the weaker water line at 325 GHz was larger than simulated line. The weak CO line at 460 GHz was observed over the shoulder of strong water line at 448 GHz. Due to the interaction between these two lines, the precise measurement of the CO concentration was difficult at the moment. In the following figure, simulations show how strongly the VMR of water can affect the transmission at CO line (460 GHz).

The transmission profile at frequencies between 410-470 GHz for flue gas is also shown in Figure 17. The simulated transmission profile for  $N_2$ - $H_2O$  mixture ( $VMR_{H_2O}$ : 0.17) at 350 °C perfectly fitted to the experimental data. This prediction was in a relative agreement with the value obtained for water vapor content of flue gas (15-20 vol%) by solving mass balances over the boiler. No CO line at 460 GHz was observed for the flue gas as expected.



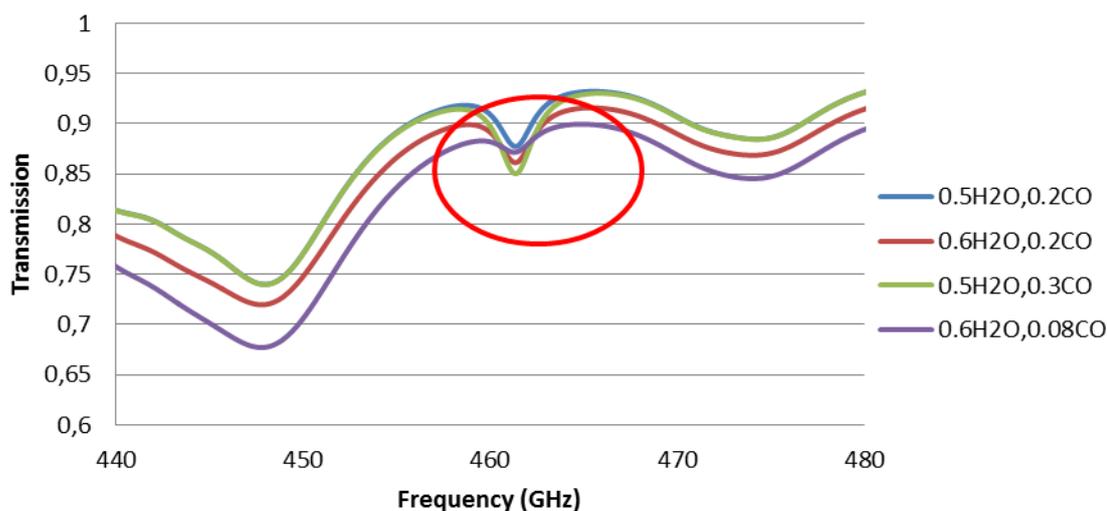


Figure 18: The interaction of water vapor line at 448 GHz and much weaker CO line at 460 GHz are proven by simulation results.

The water vapor monitoring is done with much better accuracy if the frequency is fixed and the data is sampled over tens of seconds. The expected precision i.e. minimum variation of the detectable absorption coefficient at several integration periods was determined experimentally (for the setup in its present form) and shown with dashed horizontal lines in *Figure 19*. In the figure, the calculated variation in the percentage of transmission (T) resulting from 0.01 change in VMR within the VMR range of 0.1-0.9 at 350 °C is illustrated. Apparently, the absorption line at 448 GHz is more sensitive to the variation of the water vapor concentration. Horizontal lines represent the minimum detectable changes in transmission for different levels of integration time.

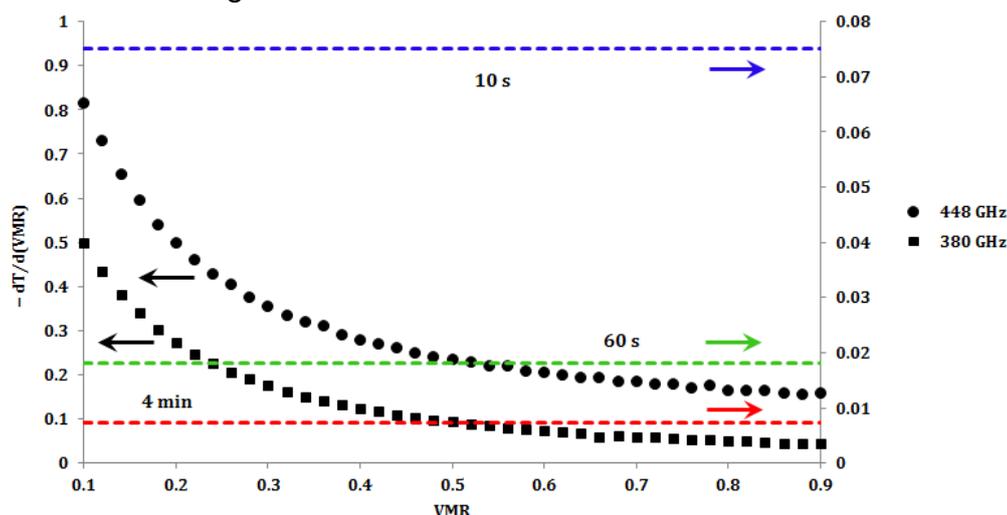
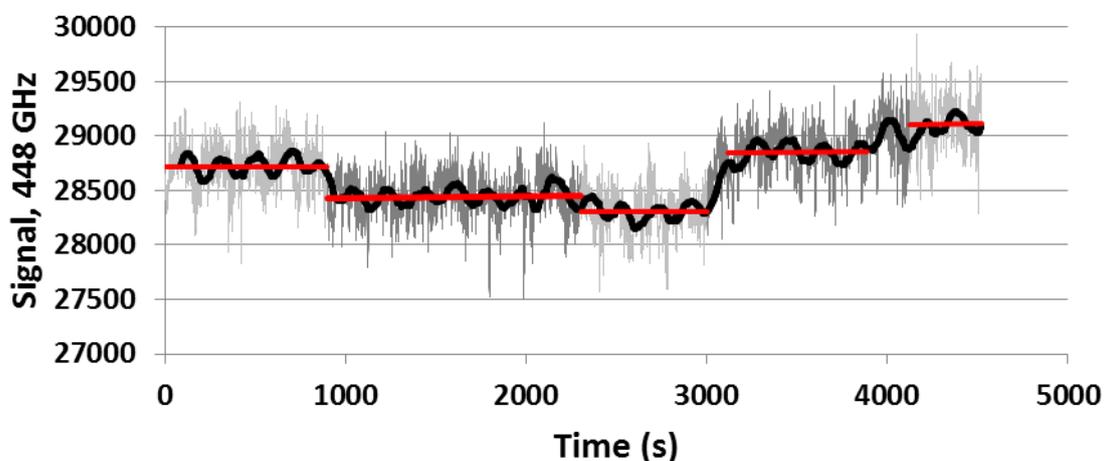


Figure 19: Horizontal dashed lines: system sensitivity to the VMR variation measured with 10s, 60 s and 4 min integration time. Symbols: simulated derivative of the gas transmission vs. gas concentration (VMR) for a VMR range from 0.1 to 0.9. Data correspond to the 380 GHz and 448 GHz water vapor lines.



According to the figure, increasing the integration time would increase the sensitivity of the system to variations in the humidity levels and in return decreases the response rate of the system. For instance, by tracing the normalized signal amplitude at 448 GHz, the current setup could detect down to 0.075% variation in absolute transmission coefficient corresponding to 0.35% VMR of water with the integration time of 10 s.

Below, is the signal monitoring curve at 448 GHz (center of the water line) during the change in steam inflow to the gasifier. Some periodic oscillations (about 1 vol% variation in H<sub>2</sub>O content within 4 min period) of the water humidity were observed. The grey lines present the online recorded data with a sampling time of 300 ms while the black solid line shows how the system was monitoring the transmission with a sampling time of 1 min. The fluctuations in the signal resemble most probably real variations in the local concentration of water vapor as well as pressure pulses in the gas mixture exposed to the THz radiation originating from the process itself. Those variations in the ratio between pyrolysis gases and steam can be expected at several time scales. At a scale of below one second due to breakup of bubbles, at a scale of 3-6 seconds due to the fuel feeding with a rotary valve and at a scale of 2-3 minutes due to boiler-gasifier interactions. By increasing the integration time to 1 min all variations with lower time scales were filtered out. The resulting curve is shown with the black solid line in *Figure 20*. The remaining fluctuations in the transmission coefficient (about 2% periodic variation in VMR of vapor with the time scale of about 3 min) were probably due to the boiler-gasifier interactions i.e. circulation of hot bed material between boiler and gasifier.



*Figure 20: Change in transmission for 5 successive levels of steam inflow to the bottom bed (i.e. 160, 200, 240, 160, 120 kg/h) vs. time.*

Following figure illustrates the variation in signal amplitude (transmission) while the gas inflow to the spectrometer switched from the raw gas to N<sub>2</sub> and then to the flue gas. The long term oscillations did not appear in this figure because the experiment was performed in a limited period of time (less than time scale of oscillations) and also because the scale of vertical axes is much larger.



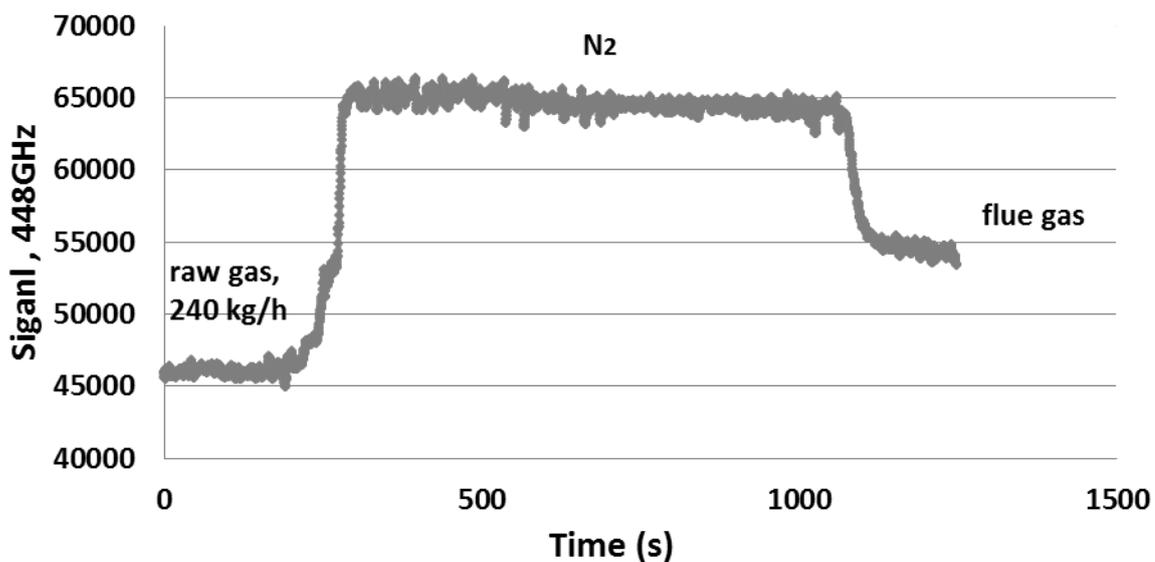


Figure 21: Signal monitoring curve at the center of water line 448 GHz while the system inflow was switching from raw gas to N<sub>2</sub> and flue gas.



#### 4. Conclusions

With this project we demonstrated a feasibility of a precise online monitoring of water vapor concentration mixed with numerous combustible gases at high temperature in both laboratory and industrial conditions. We observed good correspondence of the water vapor measurements between the THz spectrometer and more conventional offline methods. Main findings of the project can be summarized as follows:

- a) The mechanical construction of THz gas cell was well suited for high temperature gas handling (sealing, temperature uniformity, heating efficiency).
- b) Several materials were verified as THz windows, and the chosen crystal quartz was well fitted for both high temperature and low loss at the THz range.
- c) Measured high temperature absorption of water vapor and CO was in good agreement with the simulated spectra.
- d) Present state of the setup was sufficient for monitoring of water vapor variations down to 1% with an integration time below 1 min.
- e) CO lines were easily observed in a dry gas mixture, but could also be detected with a reduced accuracy even with high water vapor concentrations.
- f) Other constituents of the raw and flue gases did not disturb THz spectra.
- g) By upgrading the setup (mostly to the THz detector) the response time of the systems could possibly be reduced, and it will make the system more robust and compact.
- h) Present databases seem to lack precise data on the gas absorption lines for temperatures above 800 °C. Therefore, laboratory investigation of this matter would be required in future.
- i) Investigation of the system performance above 400 °C would be highly desirable in future.



## 5. Acknowledgements

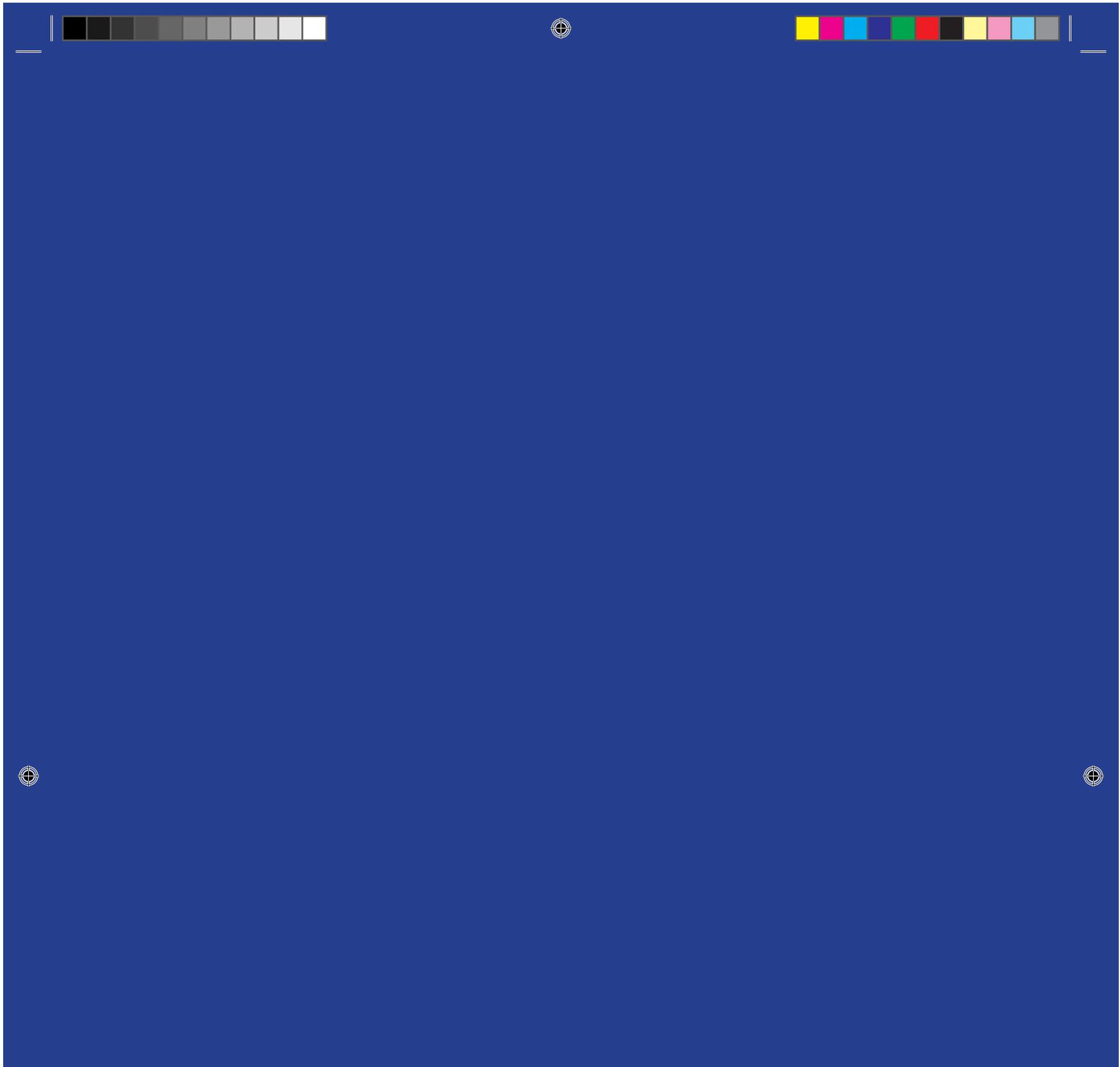
This project has been financed by the Swedish Energy Agency and the gas industry through SGC. The operation of the gasifier has been possible by support from Göteborg Energi, Metso, Akademiska Hus and Swedish Energy Agency. We thank Johannes Öhlin and Fredrik Lind for their assistance during the onsite experiments.



## 6. Literature

Rothman, L.S., Gordon, I.E., Barbe, A., Benner, D.C., Bernath, P.F., Birk, M., Boudon, V., Brown, L.R., Campargue, A., Champion, J.P., Chance, K., Coudert, L.H., Dana, V., Devi, V.M., Fally, S., Flaud, J.M., Gamache, R.R., Goldman, A., Jacquemart, D., Kleiner, I., Lacombe, N., Lafferty, W.J., Mandin, J.Y., Massie, S.T., Mikhailenko, S.N., Miller, C.E., Moazzen-Ahmadi, N., Naumenko, O.V., Nikitin, A.V., Orphal, J., Perevalov, V.I., Perrin, A., Predoi-Cross, A., Rinsland, C.P., Rotger, M., Šimečková, M., Smith, M.A.H., Sung, K., Tashkun, S.A., Tennyson, J., Toth, R.A., Vandaele, A.C., Vander Auwera, J., 2009. The HITRAN 2008 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer* 110, 533-572.





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