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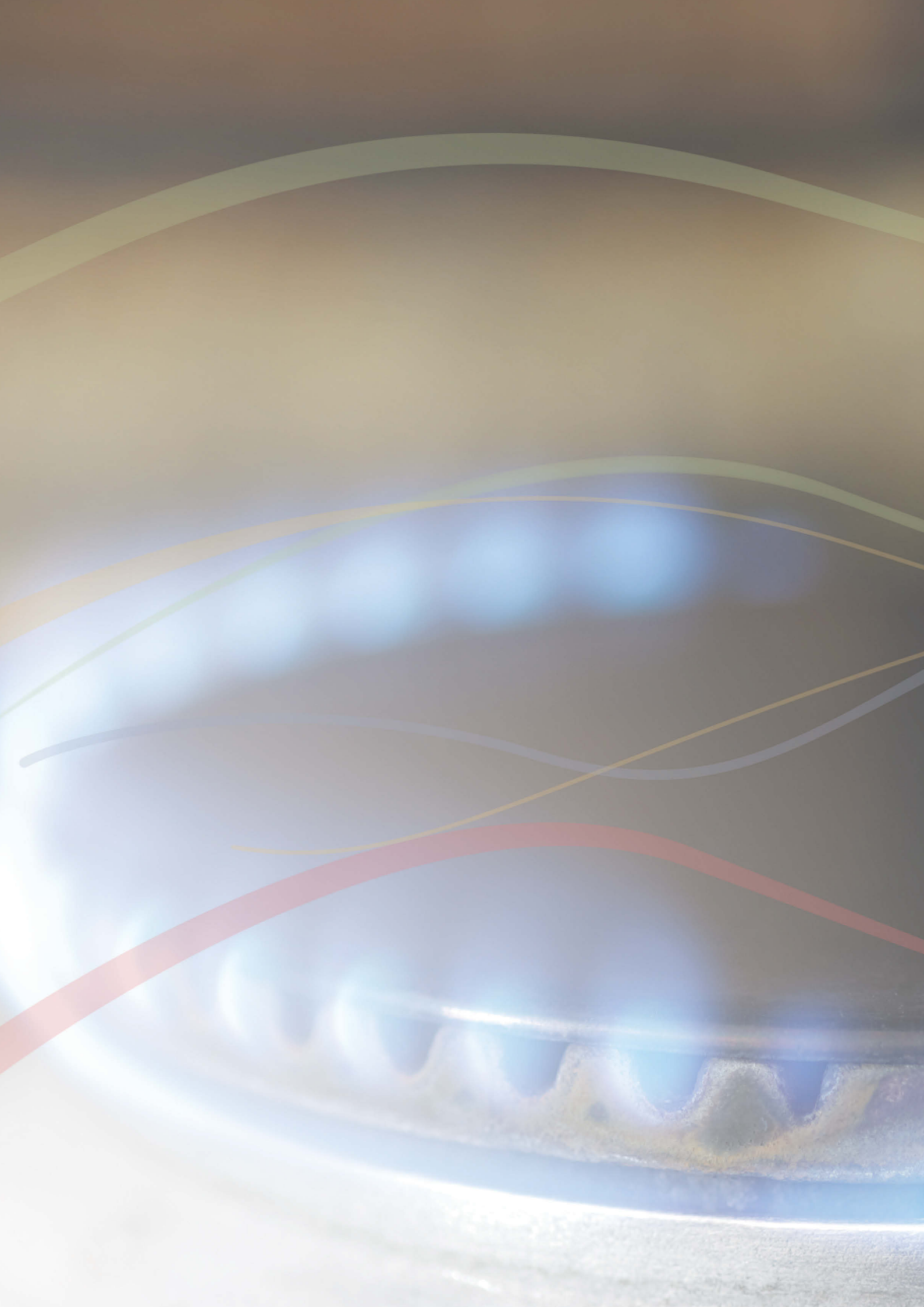

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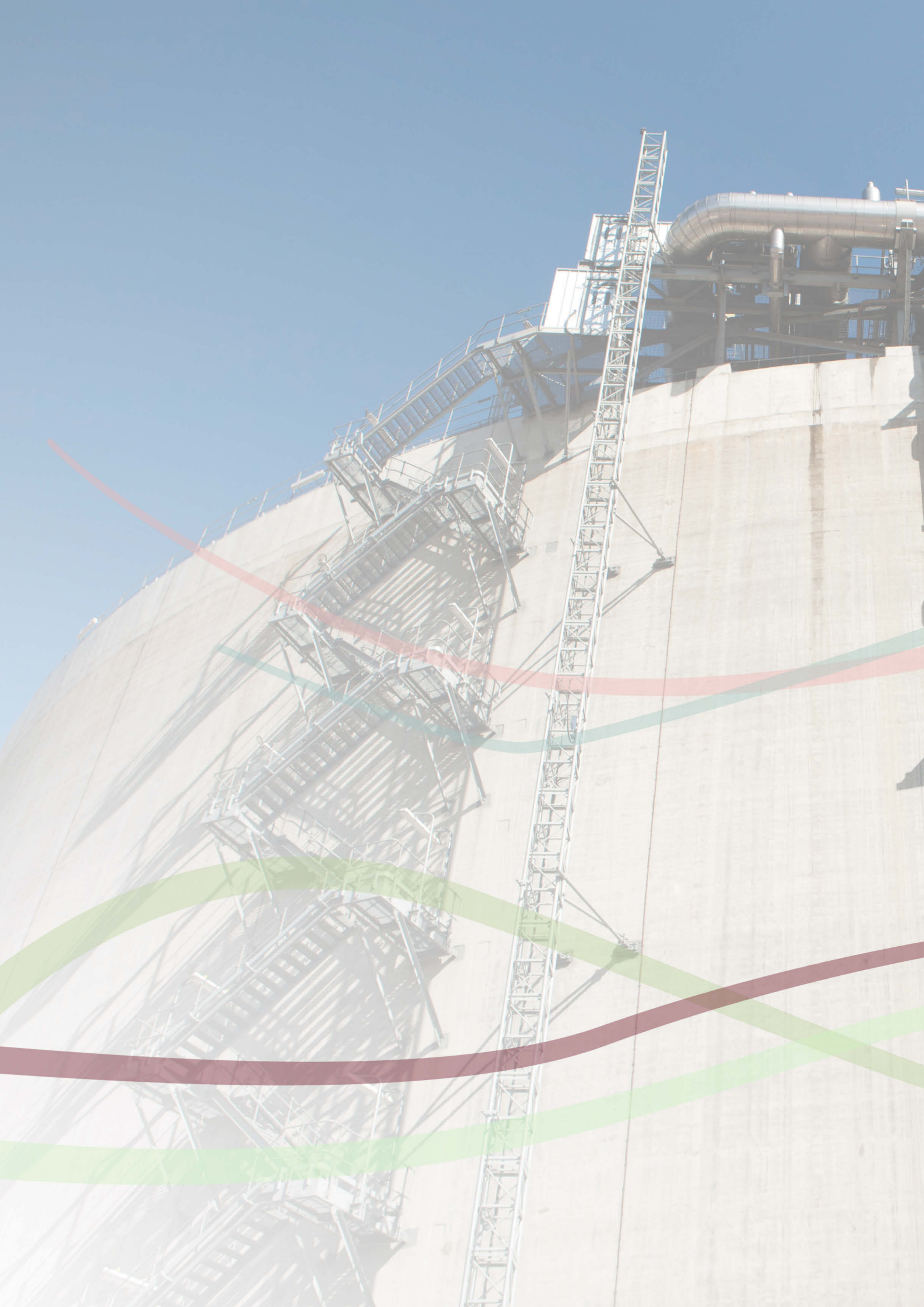

ARE THE "SAFE" CCS TRANSPORT RECOMMENDATIONS REALLY SAFE?

Authors – Bjørn Morland, Malgorzata Halseid, Arne Dugstad (Institute for Energy Technology, IFE, Norway)

The oil and gas industry uses CO2 for enhanced oil recovery, and has more than 30 years of experience with CO2 transport in land based pipelines. Based on this longstanding experience, the part of CCS (Carbon, Capture and Storage) related to safe transport of CO2 is assumed to be straight forward. However, the CO2 captured and transported in CCS comes from flue gas and various industrial sources. Unlike the CO2 transported in the existing pipelines, this CO2 is likely to contain impurities like SOx, NOx, O2 H2S and CO in addition to H2O. These impurities can cause corrosion, dust and/or solid formations, and may lead to operational difficulties. A number of CO2 specifications and recommendations for maximum impurity concentrations have been published, of which the DYNAMIS and NETL recommendations are most commonly referred to. Surprisingly, in a recent review1 from IFE there was hardly found field experience and experimental data that actually support these recommendations.

To meet the need for experimental data from dense phase CO2 systems with low levels of impurities, a new test lab was built at IFE2. The lab is equipped for experiments both in loop and autoclave systems, and with full control of multiple impurity injections. We have tested some selected CO2 compositions with impurity concentrations below the maximum ranges given in the DYNAMIS and NETL recommendations with respect to corrosion and bulk phase reactions. These experiments were performed in a rocking autoclave system with a sliding sample holder, designed to allow for continues feed of CO2 and multiple impurities (H2O, H2S, O2, NO2 and SO2) at low ppm, and for online measurements of the consumption of the these impurities. The experiments were run in dense phase (100 bar CO2 pressure at 25 and 45 °C).

We found that formation of a \free acid phase containing both sulphuric and nitric acid occurred when the dense phase CO2 contained even small amount of H2O, O2 and SO2 or NO2. Furthermore, when both NO2 and SO2 were present, the lead chamber reaction occurred, where NO2 catalysed the oxidation of SO2 to form sulphuric acid. These acid formations resulted in localized corrosion attacks. Elemental sulphur was also observed when H2S was present, and the stoichiometry of this reaction resembles that described by the Claus reaction, and was possibly catalyzed by NO2. Depositions of elemental sulphur on the pipe wall or in the reservoir are likely to cause increased corrosion and reduced injectivity, respectively.

In conclusion, we demonstrate that impurities even below the recommended maximum levels can greatly influence the corrosion and solid formation, and hence may affect the lifetime of the pipelines. These results highlight that lack of fundamental data and understanding of impurity interactions makes it difficult to define a safe operation window for transport of dense phase CO2. This emphasizes the need for dedicated experimental studies on which safe recommendations can be based.

1 Dugstad, A., & Halseid, M. (2012). Internal Corrosion In Dense Phase CO2 Transport Pipelines - State of the Art And the Need For Further R&D. NACE International.
2 http://www.ife.no/no/ife/filer/ife_brosjyrer/ife-co2-centre

BIOGAS UPGRADING PROCESS BASED ON CRYOGENIC DISTILLATION

Authors – S. Fontanils, University of the Basque Country
Sponsor – Jesus Requies, EDP Naturgas Energia

Biogas is produced when organic material is decomposed under anaerobic conditions. It can be spontaneously produced in landfills or it can be generated under controlled conditions in digester chambers. Biogas is primarily composed of CH4 and CO2 with smaller amounts of H2S and N2 and can also contain traces of other substances such as H2, O2, siloxanes, etc. Biogas can be used as vehicle fuel or can be injected into the natural gas grid. In both cases an appropriate upgrading of the biogas (CO2 removal) is required. The upgraded gas, characterized by a higher content of methane, is called biomethane.

The aim of the present work is to design a biogas upgrading process based on cryogenic distillation in order to obtain biomethane that it can be used as vehicle fuel or can be injected into the natural gas grid.

The biogas upgrading process was designed by a chemical process simulation Aspen Plus. This software requires an appropriate method to successfully simulate the process. To increase the accuracy of the simulation, the reliabilities of three equations of state were studied with Aspen Plus. The equations of state included in the study were: Peng-Robinson (PR), RedlichKwong (RK) and Soave-Redlich-Kwong (SRK). The vapor-liquid equilibrium of the CO2-CH4 mixture at different temperatures was calculated using these EOSs and the calculated results were compared with experimental data.

Once a suitable equation of state was selected, the biogas upgrading process was designed. In order to design the cryogenic process in the most economical way and to ensure maximum energy efficiency, different configurations of the process were analyzed.

The first designing step of the cryogenic process was focused on the cryogenic distillation column. In order to optimize the distillation column, parametric analyses were carried out so as to study the effect of different parameters on the mole fraction of CH4 in the distillate such as the feed stage location, the number of stages, the molar reflux ratio, the distillate to feed ratio and the feed temperature and pressure. Besides, it was of interest to make the tower as energy efficient as possible. To this end, the influence of these parameters on the reboiler duty was also studied.

Regarding to the cooling and compressing units, different schemes were studied and the final model was selected on the basis of the minimization of the energy use and economic costs.

Finally these two models, for compressing and separating of biogas, were put together to achieve the final separation model.

In addition, the obtained biomethane was compressed till 300 bar and it was evaluated if problems associated with extreme external temperatures occurred.

The first results obtained showed that the equation of state Peng-Robinson was superior to RK and SRK so it was concluded that it was the appropriate equation for the design of the biogas upgrading process.

The biogas upgrading process, comprising a cryogenic distillation column and a compression and refrigeration system, was designed and optimized achieving a final model characterized by a low energy consumption and significant economic savings.

CO2-RICH SYSTEMS IN CCS: IMPACT OF IMPURITIES ON THERMO-PHYSICAL PROPERTIES AND DEHYDRATION REQUIREMENTS

Authors – Mahdi Kapeth, Antonin Chapoy, Bahman Tohidi (Heriot-Watt University)

Over the past few decades the effect of human contribution on global warming has become ever clearer with the emission of Carbon Dioxide (CO2) being a major contributor. Furthermore the growth in global demand for energy, particularly from East Asia, has led energy suppliers to exploit natural gas reservoirs previously deemed un-economical. CO2 is a common constituent of natural gas, commonly accounting for less than 1% of the natural gas streams; however reservoirs in the Gulf of Thailand are currently producing gases with significantly high concentrations of CO2. Natural gas also contains large amounts of water when produced which can lead to issues such as hydrate formation, as well as the possibility of corrosion.

CO2 originating from capture processes is generally not pure and can contain impurities such as N2, H2, CO, water, SO2, NO2, Ar. The presence of these impurities leads to challenging engineering and flow assurance issues, as well as an increase in the significant processing costs. Furthermore, the gaseous CO2-rich stream is generally compressed to be transported as liquid in order to avoid two-phase flow and increase the density of the system. The presence of the above impurities will also change the physical properties of the stream thus affecting the compression requirements.

In this communication we present experimental techniques, equipment and thermodynamic models developed through the first phase of a Joint Industrial Project sponsored by 8 companies investigating properties of systems with high CO2 concentrations. These measurements combined with an adequate thermodynamic model can be used to set the dehydration requirements needed to avoid hydrates and/or water condensations during fluid transportation. Some experimental results on the phase behaviour and thermo-physical properties of a CO2-rich fluid such as frost points, IFT, density, viscosity...will also be presented and discussed.

DETERMINATION OF HEAT CAPACITIES, ADIABATIC COEFFICIENT AND EQUATION OF STATE THROUGH SPEED OF SOUND MEASUREMENTS IN UNCONVENTIONAL ENERGY GASES

Authors – Fernando J. Perez-Sanz
Supervisor - José J. Segovia

Natural gas is together coal and oil, one of the most important energy sources used nowadays. All three are non-renewable fossil fuels with important impact in environmental issues like global warming and greenhouse effects [1]. New energy gases have appeared lately to reduce those effects. Biogases produced in bioprocesses or coal bed methane are some of these gases. Thermodynamic characterization of those gases is necessary to improve efficiency and reduce cost in usual gas processes like compression, storage, transport, etc. There is an important lack of thermodynamic empirical data to carry out such thermodynamic characterization.

Speed of sound in gas is an important thermodynamic parameter (equation 1) which measurements provide enough information to obtain, the acoustic virial equation of state and isochoric and isobaric heat capacities as perfect gas [2].

$$u^2 = \left(\frac{\partial p}{\partial \rho}\right)_S \qquad (1$$

Where u is speed of sound, p is pressure, ρ is density and S is entropy. Equation 1 may be presented as acoustic virial equation of pressure (equation 2) or density (equation 3)[3].

$$u^2 = \frac{\gamma^{pg} RT}{M} + A_1 p + A_2 p^2 \qquad (2$$

$$u^2 = \frac{\gamma^{pg} RT}{M}\left(1 + \beta_a \rho + \gamma_a \rho^2\right) \qquad (3$$

Where γ^{pg} is the adiabatic coefficient, *R* is the ideal gas constant, *T* is the temperature, *M* is the gas molar mass, A_1 and A_2 are the second and third acoustic virial coefficient when speed of sound is function of pressure, and β_a and γ_a are second and third acoustic virial coefficient when it is function of density. Pressure and density acoustic virial coefficients are related to each other. Density values were compared to experimental values for similar gas mixture using a single sinker densimeter [4] in the same facilities. Modified Meyer's equation ($C_v = R(1-\gamma^{pg})-1$) was used to obtain isochoric heat capacity, when gas molar mass and temperature are well known.

This study carried out speed of sound measurements of several gas mixtures at different temperatures. Synthetic coal mine methane was one of the more complex mixtures measured with 10 different components. It was measured at T=250K and T=273K. Results were compared to values

obtained from GERG-2008 equation of state with discrepancies lower than 5% for the heat capacities. Experimental heat capacities uncertainty was computed to be lower than 0.15% for heat capacities and lower than 1.5% for the acoustic viral parameters. This comparison proves reliability of GERG-2008 [5] equation of state for complex mixtures.

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DEVELOPMENT OF A SMART NATURAL GAS EXPANSION MACHINE TO PRODUCE ELECTRICITY UNDER USING GEOTHERMAL ENERGY WITHOUT ADDITIONAL HEATING EQUIPMENT

Authors – Hanushan Vasuthevan (TU Dortmund University*), Dr. Andreas Brümmer*, Christian Badura (RWE Deutschland AG)

The efficient transportation of natural gas takes place with high pressure before it is distributed to the consumer with a lower pressure. Generally the reduction of the pressure in the gas grids is realized in pressure control stations with a regulating valve whereby the dissipative conversion of energy is used to heat the natural gas downstream of the regulating valve. The pressure difference potential between natural gas transport systems and the distribution systems offers a facility for electricity generation. This can be realized for example by conventional expansion machines but the temperature drops during this expansion process (Joule Thomson Effect), for which reason it is necessary to preheat the natural gas, must be balanced to prevent condensate formation and freezing in pipelines.

In this joint research project with RWE Deutschland AG, Essen, 4 the preheating of natural gas is happened just with geothermal energy **and without additional heating equipment**.

The inlet temperature in the expansion machine is fixed by geothermal energy to e.g.

T_{Inlet} = 283 K and the outlet temperature should not fall below T_{Outlet} = 273 K. After the expansion the natural gas will be reheated by geothermal energy to nearly T = 283 K again. Insofar the design criterion for this new smart expansion machine is the temperature difference not a pressure difference as usual for expansion processes.

For this application a special design of an expansion machine was essential for the whole concept. Therefore a new turbine concept must be developed. Thermodynamical simulations was carried out for this turbine to predict the inner power. Furthermore the buildup and the concept of the expansion machine are designed for a simplified integration of the electricity generation module in a pipeline. The new turbine is designed and constructed and will be produced and tested in this year at the TU Dortmund University and further tested in an existing RWE Deutschland AG pressure control station.

EFFICIENT TURBULENCE ENHANCING LOW-SWIRL COMBUSTION

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The rate of combustion in premixed natural gas flames is to a large extend controlled by the level of turbulence. In this study two different methods to generate turbulence in an efficient way are studied. This turbulence is used to increase the flame speed of a low-swirl burner. In turn, this increases its power density and makes it more suitable for gas turbine application. The reduction of more than 50% in NOx emissions as possible with low-swirl burners can then be achieved in gas turbine power generation which is responsible for a major part of the global energy conversion.

The first approach adopts an active grid that is composed of a stationary and a rotating disk with characteristic hole patterns. Upon rotation it forms a time-dependent arrangement of pulsating jets. By changing the set of disks and the rotational frequency a wide variety of flow-forcing is possible. Hot-wire measurements performed in the flow downstream of the active grid show an energy spectrum with distinct and controllable peaks. However, there is no frequency identified for the current design and parameter range where the turbulent kinetic energy or the dissipation rate is maximized. The variation in turbulent flame speed, measured by the amount of flame surface, is of the same order as the measurement uncertainty. Therefore, it cannot be concluded that the specific fluctuations introduced by the active grid are directly causing additional wrinkling of the flame front. The amount of energy in these specific scales is too low to induce a significant change in the combustion rate.

In the second approach so-called fractal grids are used to generate turbulence. These grids are obtained by truncating a self-similar fractal pattern at some level of refinement. A parametric study of fractal-grid-generated turbulence containing 24 different grids with variation in grid patterns, solidity and range of embedded scales was conducted. First, a rod-stabilized, V-shaped flame is used as such stabilization mechanism allows for considerable more variation in upstream fractal grid geometry. It is shown that fractal grids provide much more intense turbulence compared to classical grids. By increasing the range of embedded scales the turbulence is intensified. With respect to the reference case of a classical grid the turbulence intensity can be more than quadrupled while for the turbulent flame speed more than doubling is observed.

When the standard blockage grid in a low-swirl burner is replaced by fractal grids a similar increase in turbulence and combustion rate is observed as for a V-shaped flame. The turbulence is intensified when comparing the flow behind the multi-scale grid to the reference situation. This increase is expressed by more than doubling of the r.m.s. of the velocity fluctuations, while only marginal changes in pressure drop are observed. The OH-LIF experiments show an increase in flame surface density and widening of the flame brush as well as much finer wrinkling of the flame front for the cases involving a multi-scale blocking grid. The fact that the range of embedded scales mainly controls the turbulence intensity and the blockage ratio the low-swirl stabilization, engineering fractal grids for low-swirl combustion can be done with relative ease. In addition to the effect on the turbulent flame speed, it has also been verified that the low NOx emission levels, a key feature of low-swirl burners, are not affected when using fractal.

ELECTRICITY AND NATURAL GAS INTERDEPENDENCY: COUPLING LARGE MARKET MODELS

Authors – María Gil, Pablo Dueñas, Javier Reneses (Universidad Pontificia Comillas)

During the last two decades, the installation of natural gas fired power plants (NGFPPs) has increased mainly due to their low capital costs compared to other generation technologies, their high conversion efficiencies, their lower CO2 emissions, and their flexibility, which makes them well suited to provide generation in power systems with high penetration of renewable technologies. This growth of power generation based on natural gas fired power plants (NGFPPs) has lead to increasing interactions be-tween electricity and natural gas industries, and more companies are progressively and simultaneously participating as big players in both markets.

However, electricity and natural gas systems have traditionally been analyzed separately, and each company was settled in only one of the both industries. In any case, both types of companies usually support their decision-making process in market models (electricity and/or gas market models). There-fore, an energy company with a position in both markets usually has two large optimization models, (one for each system), and the communication between both models would allow companies to obtain synergies, resulting in a competitive advantage over other companies that operate uncoordinatedly in both markets.

The objective of this research is to analyze economic interactions that may arise in the medium term when a company operates in both systems. Different methods to integrate/communicate two inde-pendent optimization models (one for each system) will be discussed, as well as the possible strategic behavior of such agents operating in both markets.

GAS TRANSFORMATION FOR THE IMPROVEMENT OF H2 GENERATION PROCESSES

Authors - U. Izquierdo (University of the Basque Country)
Supervisor – Laura Barrio Cajigal (EDP Naturgas Energia)

1. Introduction

Industry is the most energy demanding sector. In general, primary sources are used in order to produce secondary ones that have higher added value and these transformations required significant amount of energy inputs. The industrial processes are well defined in order to reduce the cost of the production, by minimizing as much as possible feed and energy requirements, because this is one of the aspects that make the factories competitive. Therefore, the reduction of the energy required is considered one of the most important issues to be competitive [1].

The high price and huge amount of the energy required for raw materials transformation sectors (i.e. refinery processes, metallurgical processes...), makes the intensification of the processes to be a very challenging issue. Process intensification, in the field of chemical engineering, can be defined as "The improvement of yields and selectivities by using novel reactions or running reactions at more extreme parameters". This concept has been attributed to microreactors due to their potential to reach those targets in the field of energy technology, wherever compact and decentralized solutions are required. The concept of process intensification and the consequent use of microreactors have created the new filed known as micro-process engineering. The objective of micro-process engineering is not only to miniaturize production plants, but also to increase yields and selectivities of chemical reactions, thus reducing the cost of chemical production. This goal can be achieved by either using chemical reactions that cannot be conducted in larger volume, or by running chemical reactions at parameters (temperatures, pressures, concentrations) that are inaccessible in larger volume due to safety constraints [2]. In this work carried out, the valorisation of different feedstocks was studied (methane, natural gas and biogas) to produce hydrogen through the existing reforming processes. The interest for hydrogen is increasing and extensive research is being carried out to search new and competitive techniques for its production. This work, apart from being focused on the production step by the use of different feedstocks, it has been developed by using different type of reactors; on one hand the fixed bed reactor was used as a conventional reaction system and on the other hand, microreactors as advanced reactor systems. Therefore, this work focuses on the development of conventional and advanced reaction systems for hydrogen production from biogas, methane and natural gas.

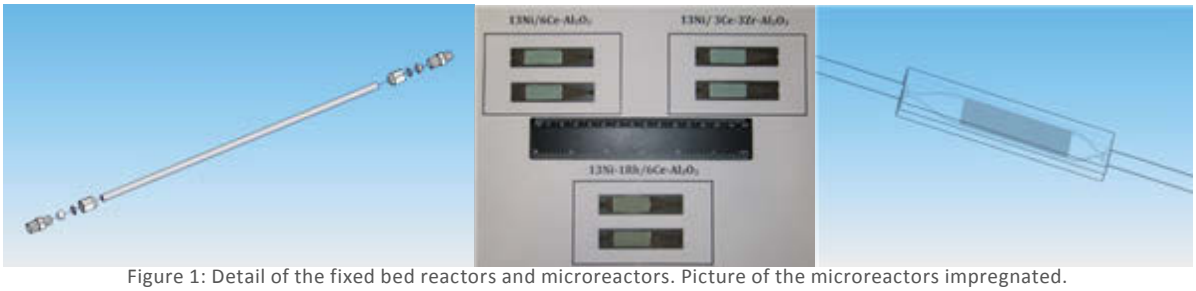

Figure 1: Detail of the fixed bed reactors and microreactors. Picture of the microreactors impregnated.

2. Experimental procedure

For methane and natural gas steam reforming reactions, SMR and NG SR, Ni based α-Al2O3 and MgO catalysts and γ-Al2O3 based noble metal catalysts (Pd and Pt) were prepared. For SMR experiments, a standard feed mixture consisted of CH4:H2O:N2 = 1:1:1.88 (molar ratio) was fed into both reaction systems at atmospheric pressure. In addition, tests at S/C ratio of 1.5 and 2.0 were also carried out in order to obtain higher conversions and minimize the coke formation. The temperature was varied between 973 K and 1073 K, rising for 50 K after each previous experiment. In the case of the NG SR experiments, a synthetic NG with the following composition was used: 87 % methane, 8 % ethane, 2 % propane, 0.5 % butane, 2 % nitrogen and 0.5 % carbon dioxide (vol.) [3].

In the case of the experiments carried out using a model biogas, the biogas consisted of 60% CH4 and 40% CO2 (vol.). A certain amount of biogas was fed in order to achieve the WHSV of 75 h-1 for dry reforming, DR, experiments. The tests were carried out at 1073 K and atmospheric pressure. For biogas steam reforming process, BSR, experiments with S/C ratios from 1.0 to 3.0 were performed. In the case of biogas oxidative reforming process, BOR; O2/CH4 ratios from 0.125 to 0.50 were tested. Finally, for tri-reforming process, TR, O2/CH4 ratios of 0.25 and 0.50, as well as increasing S/C ratios from 1.0 to 3.0 were studied. Depending on the oxygen flow, nitrogen was also fed in order to simulate an air stream [4-5].

For all the feedstocks studied, once the experiments were carried out in a fixed bed reactor system, the most stable and active catalysts were selected to be tested in the microreactors at the same conditions. Using these innovative systems and operating with them at the same temperature, pressure and reactants flow, an increase in the weight hourly space velocity, WHSV, was measured due to the needed lower catalysts amount. A bench-scale

Microactivity plant (PID Eng&Tech), was used for activity tests. The feed mixture gases flows were adjusted by electronic controllers and a High Performance Liquid Chromatography, HPLC, Gilson liquid pump was used for the deionized water injection.

3. Results and discussion

Among the catalysts tested under SMR and NG steam reforming condition, a homogeneous distribution and small particle size was reached for the Ni/MgO and Ni/Al2O3 ones. For these two catalysts evidence of a uniform nickel particles distribution was observed as well as the catalytic surface which was free of carbon. The presence of Ni particles in the catalytic surface of these two micrographs was confirmed by backscattered electron imaging. Moreover, in the case of Ni/MgO catalyst, a smallest particle size (15-60 nm) was measured when compared with the Ni/Al2O3. In addition, for the Ni/MgO catalyst deactivation by sintering was not measured as the original particle size was 28.5 nm (measured by XRD). For Pd/Al2O3 and Pt/Al2O3 catalysts, SEM images were taken from secondary electron detectors in order to study surface morphology. In the surfaces of both Pd/Al2O3 and Pt/Al2O3 catalysts carbon filaments growth were observed. Therefore, the low activity measured for both noble metals catalysts can be attributed to the carbon filaments growth covering the catalytic surface.

When biogas was valorised for producing hydrogen by means of DR, BSR, BOR and TR processes, high methane and carbon dioxide conversions were reached by all tested catalysts and studied processes using the fixed bed reactor. The Rh-Ni/Ce-Al2O3 catalyst achieved the highest hydrogen production yield in DR reaction. However, this process requires huge energy supply and carbon filaments growth was observed by SEM. For the BSR process, increasing the S/C ratio lower carbon dioxide conversions were measured, which implied a decrease of the hydrogen yield. Consequently, at S/C=1.0 were measured the best results. In the case of BOR process, the maximum hydrogen yield was obtained at O2/CH4=0.25, which corresponds to intermediate values of methane and carbon dioxide conversions. The highest hydrogen yield and H2out/COout molar ratio were obtained using Rh-Ni/Ce-Al2O3 and Ni/Ce-Zr-Al2O3 catalysts. Regarding biogas TR process, different O2/CH4 and S/C ratios were tested. For this process, at O2/CH4=0.25 and S/C=1.0 the bimetallic catalyst reached the highest carbon dioxide conversions and hydrogen yields. Operating with microreactors, conversions similar to the ones measured using the fixed bed reactor were achieved, being the Ni/Ce-Al2O3 catalyst the one producing the highest hydrogen yield when operation under the conditions specified for BOR.

4. Conclusions

In this work the microreactor system was used in order to study several processes intensification. It has been demonstrated that biogas, methane and natural gas transformation was able to run at much higher WHSV with the benefit of reducing energy inputs and catalysts amount when microreactors were used. This evidence leads to go further in the research and development work using the advanced reaction systems.

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GAS-FIRED COGENERATION AND DISTRICT HEATING IN BELGIUM: BARRIERS AND OPPORTUNITIES

Authors – Kris Poncelet, Juliana Zapata Riveros, William D'haeseleer (University of Leuven)

Gas-fired Combined Heat and Power (CHP) plants can potentially contribute to attain the "20-20-20" targets set out in the Climate and Energy Package to reduce the EU greenhouse gas emissions with 20% with respect to 1990 emission levels by increasing the share of renewable end energy use to 20% and improving the EU energy efficiency by 20%.

Gas-fired district heating systems could contribute to reaching each of these objectives by increasing energy efficiency or by facilitating the uptake of renewable energy sources. In this context, this work tries to give a realistic estimate of the CO2-emissions savings that can be obtained by implementing Combined Heat and Power District Heating (CHP-DH) schemes in Belgium

The decision criterion employed to assess the potential of CHP-DH is the total additional cost of introducing district heating compared to a reference scenario in which heat is produced by means of a domestic gas boiler and electricity taken from the electric grid. Additionally, an emission abatement cost is estimated, this cost facilitates the comparison among different potential CO2-reduction technologies.

In order to incorporate the dynamics of the CHP plant with the electricity production park and obtain realistic values of the fuel and emission savings that could be obtained by implementing DH schemes, an integrated dynamic analysis based on the mixed integer linear programming (MILP) implementation of the unit commitment model is performed. The unit commitment problem determines the most economical-optimal schedule of the generation units that satisfy the electric demand.

Furthermore, a scenario analysis is done to study the performance of different CHP-DH technologies such as gas turbines (GT), Internal Combustion Gas Engines (ICGE) and Combine Cycle Gas Turbines (CCGT).The results show that CHP-CCGTs obtain the highest emission savings (around 120 ton/GWhth) and that the use of thermal energy storage strongly increases the obtained savings.

Nevertheless, the fuel and emission savings are not sufficient to counterbalance the higher investment cost and operational expenditures associated with DH. This is translated in large DH emission abatement costs (up to 396 €/ton using GT and thermal storage), which are higher than the projected emission allowance price of 28,74 €/ton.

Finally, a sensitivity analysis shows that a variation in the investment cost of the heating network and the cogeneration unit have a large impact on the feasibility of district heating, as well as the gas and emissions allowance prices.

GASIFICATION OF POULTRY LITTER – WASTE TO ENERGY

Authors - D.S. Pandey, M. Kwapinska, J.J. Leahy, W. Kwapisnki (University of Limerick)

Biomass is regarded as a renewable source of energy for future. The thermochemical conversion of biomass is one of the most promising forms of future clean energy. Dry agricultural residues (straw, poultry litter, and compost) present opportunities for renewable energy production in Ireland. It is estimated that production of poultry litter in Ireland is approximately 140,000 tonne per annum with approximately 1.26 PJ per annum energy resource (Abelha et al., 2003 and SEI). Poultry litter consists of a mixture of bedding material, feathers, manure, urine and food particles. Thermochemical (combustion, pyrolysis and gasification) and biochemical/biological (digestion and fermentation) route can be used for energy generation from poultry litter. Also, the European Parliament has unanimously adopted EU Regulations (1069/2009) for the use of poultry manure as a fuel for on farm energy production. Among them gasification offers flexibility for heat and power generation from biomass derived syngas.

An equilibrium model based on minimization of Gibbs free energy are developed .The study focuses on prediction of product gas composition and heating value of poultry litter. It provides a substantial understanding of the various operating parameters on the gasification process. Based on the model results, the optimum conditions that would yield a maximum conversion for the poultry litter gasification process have been identified.

The equilibrium model predictions enable comparisons with experimental dataset and the limitation of equilibrium model will be discussed. In particular, characteristic of poultry litter are identified as well as further need of model refinements to catch the most essential processes occurring during the gasification process. The proposed thermodynamic equilibrium model improves the understanding of poultry litter gasification process and can be used as a predictive tool while refining and updating the model as well as at the optimization stage.

METHANE STORAGE IN POROUS ACTIVATED CARBONS

Authors – Andras Perl, W.J.T van Gemert

Methane is a prominent alternative energy source for transportation1 and it is a potential energy carrier for the transition from today's fossil fuels-driven economy to a renewable energy-based one2. It is considered a cleaner fuel because it generates less carbon dioxide and sulfur oxide than other fossil fuels.

The main hindrance in its wide usage as transportation fuel is the low volumetric energy density of the gaseous material. The need to increase the volumetric energy density of the adsorbed methane drove the main research efforts in the last decade. The two common and currently used methane storage methods, liquefaction at low temperature and compression to 200-300 bar at room temperature, require expensive cryogenic vessels or thick-walled cylindrical storage vessels and multi-stage compressors. Adsorption in porous materials could enable a simpler, safer and cost-effective method for storing methane at ambient temperature and at reasonably low pressure. A single stage compression step can generate around 40 bar,3 making this pressure a practical benchmark for storing by adsorption. Methane adsorption in porous solids at supercritical conditions mainly occurs in the micropores of the adsorbing material and adsorption capacity increases with the micropore volume.4

Within the Energy Delta Gas Research (EDGaR)5 project, advanced gas storage technologies, such as methane adsorption, are examined. An experimental setup is designed and built to characterize methane adsorption. We study and test the main thermodynamic and kinetic characteristics of methane adsorption and desorption on activated carbon. Both experimental measurements and theoretical calculations are performed to enhance our knowledge about the general performance and the cyclic behavior of the adsorption and desorption processes. The experimental results are used to validate the theoretical model and calculations will be performed to study the feasibility and performance of a full scale adsorption reactor.

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PREHEATING OF PROCESS GASES: ADVANCES AND LIMITATIONS FOR THE STEAM REFORMING CASE

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Supervisor – Dr. Dimosthenis Trimis (Technische Universität Bergakademie Freiberg)

Preheating of conventional process gases for thermochemical conversion applications by excess heat enhances the efficiency of the whole system. Main components of such gas compositions are short-chain alkanes (<C4), whose given contents influence the preheating potential significantly. Methane can be preheated unproblematically to higher temperatures due the thermodynamic stability. However, C2-C4-alkanes as present in LPG or in natural gases (>20 vol.-% [1]), limit the possible preheating temperatures substantially. Main reason for this limitation is the tendency for the formation of carbonaceous deposits in the system caused by unwanted prereactions like the pyrolysis of hydrocarbons that are initiated by preheating. A noticeable cracking of C2-C4-alkanes into unsaturated hydrocarbons occurs at temperatures above 450°C in inert atmosphere. Furthermore, in case of interaction of alkanes with catalytic active tube materials significant crack- and dehydrogenation reactions take place at temperatures below 250°C. Resulting decomposition products influence following catalytic processes negatively and lead to rapid deactivation. This is among others the case in the actual relevant application of small scale fuel cell systems, where production of hydrogen rich synthesis gas by catalytic steam reforming takes place. Published reaction mechanisms of hydrocarbon pyrolysis are designed primarily for high temperatures (>700°C). For this reason the mechanisms in low temperature regions in connection with a strong dilution of steam are only limited suited.

The aim of this work was to demonstrate the potential of unwanted prereactions in low temperature regions and to compare the results with published reaction mechanisms. Furthermore, the negative influence of unsaturated hydrocarbons on reforming catalysts could be shown by using Temperature-Programmed-Methanation (TPM) and different carbonaceous deposits could be identified. Finally, measures for reduction of deposits are formulated and investigated. Such measures are hydrogen recycle, addition of air and preheating of hydrocarbon feed with overheated steam.

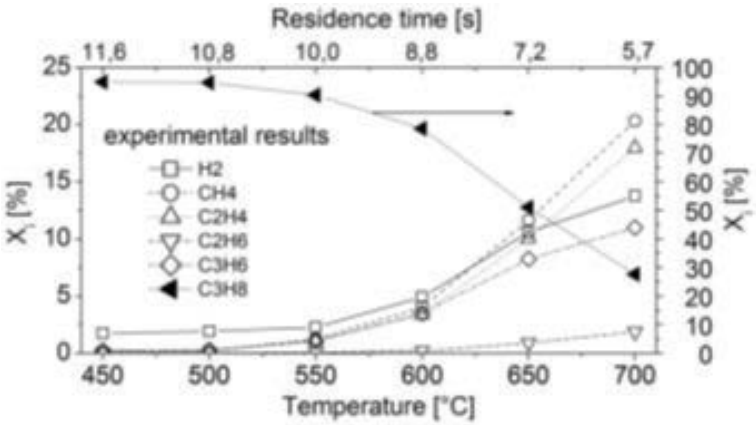

Figure 1 Pyrolysis of pure C3H8, product gas composition, own measurements in a plug flow reactor

PRODUCTION AND PURIFICATION OF HYDROGEN USING DRY REFORMING AND STEAM IRON PROCESS IN A FIXED BED REACTOR

Authors - M. Herrer, J. Plou, P. Duran, J. Herguido, J.A. Peña (Universidad Zaragoza)

1. Introduction

The progressive depletion of fossil fuels is promoting the research on new renewable sources of energy. Hydrogen is a strong candidate to replace energetic dependence of fossil fuels because it is a clean and renewable energy vector. Nowadays, hydrogen is mainly used in petrochemical and basic chemicals applications. This production scenario is not compatible with the new energy requirements (economic, clean and renewable source) and its use in fuel cells applications. Therefore it is necessary to increase the available hydrogen production methods. Due to its high methane content, biogas can be envisaged as suitable feedstock for hydrogen production. Biogas is the product of anaerobic digestion of solid municipal wastes, sewage sludge, agricultural wastes and dedicated crops or livestock wastes.

Present research focus on the combination of catalytic dry reforming of biogas with steam iron process in order to generate high purity hydrogen bearing in mind the concept of process intensification. By MDR, a synthetic mixture of a sweetened biogas (CH4 and CO2 ratio 50:50) catalytically reacts producing a gas mixture consisting of CO, H2. Also solid carbon deposits over surface of the solid. In the same vessel (catalyst and reactive solid is mixed up homogeneously within), the emerging syngas reduces the iron oxide to metallic iron (step 1). During the following step (step 2), this metal is forced to react with steam to release pure hydrogen. This cyclic process comprising two consecutive steps is called “Steam iron process” -SIP- [1]. The exhausted gases obtained during step 2 are hydrogen and unreacted water, easily separated by condensation.

2. Experimental

The experiments were carried out in a packed bed reactor. The solid used (2.5g) was a mixture of 67.5%wt additivated oxide, 7.5%wt Ni based catalyst and 25%wt silica. The doped oxide was synthesized in lab. It is Fe2O3 based oxide additivated with Al2O3 and CeO2. Alumina provides structural stability and ceria enhances reaction rates where oxygen migration is involved. The synthesis was performed via citrates [2]. On the other hand, the catalyst is a non-stoichiometric nickel aluminate with nickel in excess. It was synthesized by co-precipitation with ammonia using increasing pH method [3]. In this way, two phases were obtained: NiO and NiAl2O4. Only after in-situ activation by NiO reduction, metallic nickel can catalyse the reaction. The gas fed in reduction step was 0.125 bar of CH4; 0.125 bar of CO2; 0.75 bar of Ar as inert. This composition emulates a real sweet poor biogas stream with low methane content. Oxidation step was always performed at 500 ºC, using a partial pressure of 0.25 bar of steam (conditions optimized in previous studies) [4]. Total flow for both steps was 250 NmL/min. Exhaust gases were analysed by two instruments in parallel: a gas chromatograph and a mass spectrometer. The main purpose of this setup was collecting real time composition of gases distribution (MS) with in-situ calibration (GC).

3. Results and conclusions

Some process parameters were studied as the effect of temperature over reduction step (temperature from 600 to 750 ºC at 50 ºC interval), effect of partial pressure of biogas (ratios CH4:CO2 of 50:50, 65:35 and 70:30). These conditions affected also the subsequent oxidation. The feasibility to produce and purify bio-gas mixtures was achieved, and it was possible to obtain optimal conditions for the process. A suitable temperature for reduction step was found to be between 650 and 700 ºC, where maximum methane conversion and low carbon formation takes place. Partial pressure of CH4:CO2 of 50:50 at optimal temperature was the best choice because an increment in methane composition produces increment in coke deposition and

possible operational issues due to overpressure effect along the fixed bed. During oxidation steps at optimal reduction temperatures, generation of high purity hydrogen was demonstrated due to the inert behaviour of carbon formed along the previous reduction step. Neither CO nor CO2 were detected by GC during oxidation what implies low content of these species in the exhaust gases, always well below 1%v.

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RECTIFICATION OF BIOGAS WITH LOW PURIFICATION LEVEL BY HYDROGEN ADDITION

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Supervisors – Laura Barrio (EDP Naturgas Energia)

Introduction

The addition of different mixtures of biogas and hydrogen to a reference natural gas is studied in this project, so as to establish interchangeable mixtures that can be directly injected into the gas grid with the final aim of direct combustion in gas appliances. In this work, the effect of the addition of high-CO2-content biogas to the conventional natural gas is studied, the problems of flame detachment being assessed. On the other hand, the opposite problem of light-back process produced by the addition of hydrogen to the natural gas is determined. As a consequence, the possibility of simultaneous addition of hydrogen and none highly purified biogas to the conventional natural gas is explored and the synergistic effect of the two additions evaluated. With this proposal the cost of the biogas depuration processes prior to grid injection could be reduced with the consequent economical save. Moreover, due to the use of two renewable energy sources (biogas and hydrogen) the contribution to a lower environmental impact is noticeable.

Technology procedure

Although the legislation in force requires a 95% of pure methane in volumetric content to allow the direct injection of bio-methane into the grid [1], the possibility of transport and consumption of the mixture of natural gas and biogas with lower purification levels than those which are demanded by the standard is being studied, but always respecting the Wobbe Index limits and combustion potential of the interchangeability window for the combustible gases from the second family in the Delbourg diagram. Because of the addition of biogas into the mixture the combustion potential is reduced and this effect is corrected by adding hydrogen.

Regarding the capability of the natural gas grid for the transportation of hydrogen, the Naturalhy project has proved that the security related to transport, distribution and use of the natural gas is not significantly affected when hydrogen is added up to 20% in volume [2].

Firstly, the interchangeability study is carried out using the Delbourg method, choosing a reference natural gas that satisfies the interchangeability criteria for the second family of combustible gases. Then, the same study is performed with the alternative interchangeability methods of A.G.A index and Weaver index.

Main results and conclusions

By adding variable percentages of biogas and hydrogen it is concluded that the following mixtures are interchangeable because they respect the limits of the Delbourg diagram: 5%biogas, 15% hydrogen, 80%natural gas; 10% biogas, 10% hydrogen, 80% natural gas ; 20% biogas, 10% hydrogen , 70% natural gas; 15% biogas, 10%hydrogen , 75% natural gas (% in volume). These results are also obtained with the methods of A.G.A index and Weaver index, which proves the interchangeability of the mixtures.

Hence, according to the percentages of mixtures obtained, it is concluded that biogas can be added up to 20% in volume to the natural gas, without exceeding the addition of a 15% in volume of hydrogen in any case, which ensures that the security if the grid is not critically affected.

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SIMULATION AND ANALYSIS OF GAS NETWORKS WITH NEW DISTRIBUTED GAS SUPPLY SOURCES

Authors - Muditha Abeysekera, Jianzhong Wu, Nick Jenkins (Cardiff University)

Future energy scenarios for the UK foresee a number of new bulk sources of gas that are likely to be injected into the gas distribution network. These are biomethane, shale gas, coal bed methane, products from biomass gasification and hydrogen. The new sources are likely to be geographically clustered, which could have significant implications for the distribution network management considering seasonal demand variations. The injection of alternative fuels will also alter the transportation properties (eg. Pressure) and thermodynamic parameters (eg. Wobbe index) of gas supplied. The variations can affect consumer appliance functionality and thus will require revising network management strategies. A comprehensive simulation of the gas network under varied supply scenarios is important to understand the impact of these new distributed gas sources on network management.

A model was developed to extend the steady state analysis of gas networks to include distributed gas supply sources. A case study was designed to validate the model and carry out an initial assessment of the network response to hydrogen injection at different locations. The results show that blending hydrogen has an effect on both pressure and the heat content delivered to the consumer. The location of injection determines whether the effect is detrimental or beneficial.

The model that was developed is capable of providing quantitative evidence on the technical and network management issues that would result from the connection of distributed gas supply sources. It is also possible to use the model to provide recommendations for revised or novel network management strategies.

Current research work is focused on combining the gas network model with an electrical power flow analysis in order to examine the benefits to the power network of coupling with the gas network (For example- via power to gas and CHP).

THE SIMULATION RESULTS OF OVER 1.550.000 GAS METERS CALIBRATION, UNASPECTED SITUATIONS, STUDIES TO PREVENT GAS METERING LOSS.

Authors – Cevat Ozarpa (iGDAS)

GDAŞ, İstanbul Gas Distribution Company started to operation in 1990 is the biggest gas distribution company in Turkey with 4.2 million gas meter installed and about 5.2 billion m3/year gas sale. Maintenance and replacement works have being done in order to keep these equipments on duty during the time.

Especially gas measurement equipments should be operated properly to make income of a gas distribution company balanced. All of the consumed gas amount passes through gas meters and is invoiced to the gas users. As a result, proper operation of gas meters has a direct relationship with income of gas distribution company and customer satisfaction. Meters must be maintained periodically in order to be controlled whether they operate properly. Periodical maintenance of gas meters includes below mentioned stages:

Gas meter is demounted from the line on which it is connected and parts which are connected to the installation are covered with a cap and shipped in suitable conditions. After preliminary control is made, meter is cleaned. Meter results after being conditioned in laboratory environment are calibrated and measurement results are obtained. After repairs and adjustments are made, if necessary, its numerator is reset, seal is renewed and painted. Finally these are labeled and packed to reuse.

In this study, each stage of periodical maintenance will be explained in detailed form. Especially impressive findings made after this operation related to 1.550.000 gas meters in total which are calibrated in the last five years. Some results will be given as follows; the contributions of this operation to both gas users and gas distribution companies, the information received by meter producers on field performances of their meters, how measurement precision of gas meters by years changes, approximate life of meter, why unserviceable meters which are out-of-use are scrapped, unlawful gas utilization ratio and methods(physical intervention of the subscriber to the meter).Remarkable calibration results obtained will be shown by numerical data and graphics.

PRE-CHAMBER IGNITION SYSTEM FOR HEAVY DUTY NATURAL GAS ENGINES

Authors – Ashish Shah, Per Tunestål, Bengt Johansson (Lund Univeristy)

The Gas Engine Project at Lund University aims to explore and understand the combustion phenomenon in engine operating on gaseous fuels and develop technologies as an alternative to present day diesel operated heavy duty engines which are facing severe challenges like stringent emissions norms, high technology cost and unsustainable fuel supply. The current phase of this project focuses on exploring alternative ignition techniques to further extend the limit of lean or diluted combustion to achieve better emission reduction and efficiency improvement in heavy duty natural gas engines. The project particularly focuses on pre-chamber ignition system which, based on a literature survey, seems to be very promising but its applicability to heavy duty natural gas engine for mobile application is less explored compared other alternatives like diesel pilot injection, for example.

Initially, experiments were performed to compare the performance and emission characteristics of a multi-cylinder heavy duty natural gas engine when operated with un-fueled pre-chamber spark plug and a conventional spark plug. Results showed marginal increase in operating lean limit with excess air and dilution limit with EGR, however, there was substantial reduction in the flame development angle and combustion duration while the combustion was much more stable (low coefficient of variation of IMEPg), which implied that spatially distributed jets from a pre-chamber spark plug offered a better ignition source than a single point spark. Even so, the main purpose of exploring an alternative ignition technique, which was extension of lean and dilution limit of operation, was not being served. The reason behind this was believed to be over-leaning of mixture in the pre-chamber by residual gasses in absence of any scavenging mechanism to flush the pre-chamber in the beginning of every cycle.

Following these observations, a literature survey was conducted and it was soon identified that additional fueling to the pre-chamber will help scavenge the residual gasses and will also help in forming an easily combustible mixture in the pre-chamber while the main chamber is extremely lean. There are at least two strategies of operation with fueled pre-chamber, having a near stoichiometric mixture in the pre-chamber and having a fuel-rich mixture in the pre-chamber. The later, also referred to as LAG-ignition process, is relatively less explored but has documented benefits over the former technique. However, its applicability to heavy duty engines operating with natural gas is relatively unexplored and hence was chosen for further study.

A single cylinder engine setup was then prepared which equipped fitted with a custom make pre-chamber capable of fuel injection, spark ignition and pressure measurement. First set of experiments performed were to study the effect of relative excess air ratio between the pre- and main chamber and also to evaluate the lean limit of operation with excess air. It was observed that the lean limit of combustion extended considerably from excess air ratio of about 1.7 (with un-fuled pre-chamber) to 2.6 (fueled pre-chamber) and correspondingly NOx emission reduced from about 7 g/kW.h to below 1 g/kWh. Pressure measurements from the pre- and main chamber were used to perform heat release analysis which showed that the initial rate of heat release in the main chamber increased with increasing degree of fuel rich combustion in the pre-chamber. The maximum indicated efficiency observed at operating load of 10 bar IMEPg was 47.5% at a combination of main chamber excess air ratio of 2.4 and pre-chamber excess air ratio of 0.2.

The upcoming experiments planned are to study the effect of pre-chamber volume and the connecting nozzle diameter on combustion in the pre-chamber, the resultant jets and ignition on main chamber charge.

CHEMICAL SPECIATION OF SULPHUR, IRON, COBALT, AND NICKEL IN BIOGAS REACTORS - EFFECTS ON THE BIOAVAILABILITY PROCESS

Authors – Sepehr Shakeri Yekta (Linköping University)

Iron (Fe), cobalt (Co) and nickel (Ni) are commonly supplemented to biogas reactors for improvement of biogas production efficiency, organic substrate degradation, and process stability. Cobalt and Ni are essential micronutrients for growth and activity of microorganisms. Iron addition, often in higher quantities compared to Co and Ni, is mainly carried out as a measure to control sulfide concentrations in the reactor. The stimulatory effect of metals on the performance of biogas reactors depends on biological and chemical properties of the reactor environment, where sulfur (S) chemistry plays a regulatory role in overall chemical speciation and bioavailability of the metals. Therefore, an understanding of the effects of S species on chemical speciation of metals is required to identify the main biochemical processes controlling their bioavailability, which in turn is important for devising and optimizing the metal dosage to biogas reactors. The present research addresses the interrelationship between the overall chemical speciation of S, Fe, Co, and Ni in continuous stirred tank biogas reactors (CSTBR), the most common reactor type in Sweden for industrial biogas production.

In brief, it has been demonstrated that the S to Fe molar ratio, which is commonly regulated by addition of Fe stock for sulfide removal or prior to anaerobic digestion of sewage sludge, controls the concentrations of sulfide and metal-sulfide complexes in the aqueous phase. In addition, the chemical speciation of metals in the aqueous phase is largely affected by dissolved organic matter such as thiol functional groups, which in turn affect chemical nature of the pool of soluble metal species in contact with the microbial cell surfaces. The dynamics of Co and Ni in the studied CSTBRs demonstrated different features, although both metals were strongly affected by sulfide through precipitation of metal-sulfide phases (i.e. CoS(s) and NiS(s)) and displayed a relatively similar inorganic chemistry in the aqueous phase. In particular, the results suggest that microorganisms are able to enhance the solubility of the pool of CoS(s) in the reactors for example by releasing specific Co-binding organic ligands. The vitamin B12 may be an important player in this context. The chemical speciation and solubility of Ni are mainly related to its interactions with sulfide. Complex processes which involve interactions of Co and Ni with FeS(s) (e.g. co-precipitation and adsorption) seem to contribute to the solubility of these metals as well.

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