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Virtual Measurement of Emissions from Produced Water Using an Online Process Simulator

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1 SUMMARY

In this work we present a new and accurate tool for estimation of cold flare (unburned gas vent to air) emissions from a produced water handling system on the Equinor operated field Gudrun. It is demonstrated to provide accurate virtual measurements of CO_2, methane and nmVOC emissions. The new online tool improves accuracy and traceability of emission reporting and overcomes shortcomings of the conventional method of multiplying mass of produced water with a gas solubility constant on an annual basis. The new tool is named NeqSimLive and uses the open-source process simulator NeqSim connected to real time process data.

In 2022, the reported emissions from Gudrun using the conventional method were 11 000 tonnes CO_2 equivalents. This method reports methane and nmVOC (non-methane volatile oil components) only. NeqSimLive calculates emissions also for CO_2. Compared to the conventional method, NeqSimLive calculates lower hydrocarbon (methane and nmVOC) emissions, but higher total emissions (by mass) due to inclusion of CO_2. Methane and nmVOC have higher environmental impact than CO_2, with CO_2 equivalent factors of 28 and 2.2, respectively. In sum, the new method reduces the reported emissions by more than half, to about 4 700 tonnes CO_2 equivalents.

To validate the model, the results were compared to process data from Gudrun. The produced water gas composition deviation was within ±1% for CO_2 and methane in comparison with available laboratory gas composition measurements in the period. Gas-water ratio uncertainty is estimated to be ±4% considering model sensitivity to variations in pressure, temperature and CO_2 contents, and the discrepancy between simulated and analysed water sample GWR. Virtual and Coriolis measurements were compared, and the virtual measurement underpredicted gas mass by -2 and -7.2% for the two years respectively. Gas molar mass and gas density show low deviations compared with ultrasonic flow meter readings. The new method has an estimated uncertainty of GWR, gas and CO_2 emissions of ±4%, which is within the authority requirement of ±7.5% for emission gases. The new tool has proven to give CO_2, methane and nmVOC emissions with significantly improved accuracy compared with the classical method using total produced water rates and a fixed gas solubility constant.

Online measurement of emissions is an important step to better understand emissions, identify the main sources, and to help build an action plan. The new method gives automated, online, accurate emission reporting and forms a basis for improved decision making for how to reduce emissions.

2 INTRODUCTION

Equinor has a continuous ambition to reduce greenhouse gas emissions (GHG). The goal is to reduce emissions from operated activities by 50% by 2050 (compared with 2015). Improved accuracy in emission data is a contributor on the path to meet the overall ambitions.

Gudrun is an Equinor operated field in the North Sea. For the Gudrun field one major source for these emissions is (cold) vented gas from produced water. Cold flare is the direct release of unburned gas to the atmosphere through non-ignited flare. Gudrun has been reporting the cold flare emissions assuming 100% methane and nmVOC up to recently.

Pressurized samples were taken from produced water from 1st, 2nd and test separators and sent to third party laboratory for analysis by doing a single stage flash to atmospheric conditions to measure the gas composition. The analysis confirmed that the gas composition from these samples have relatively high amount of CO_2, and previous emissions from cold flare have been over-reported. It was decided to develop a live model to verify the gas solubility in water comparing measured data with virtual simulated data.

By using the digitalisation tools available in the Equinor toolbox, NeqSim was identified as the suitable process simulator to be used for developing a digital twin for reporting the emissions from the produced water at Gudrun. NeqSimLive process tool is based on fundamental thermodynamic and unit operation models for accurate process simulation of oil and gas processing. The tool is simulating real-time performance monitoring with live process data from offshore production facilities and compositions measurement. A description of the thermodynamic model used for calculation of gas solubility in Appendix A.

The application is continuously providing virtual measurements and fluid analysis compositions, and a typical use case is to provide measurements where instruments are not available or uncertain.

3 REPORTING OF PRODUCED WATER EMISSIONS

Methane and nmVOC emissions from offshore oil and gas platforms and infrastructure are monitored and reported in accordance with the regulations set by the Norwegian Environment Agency. Operators of offshore facilities are required to submit emission data to the authorities. According to [1] *"the operator shall measure or calculate emissions and discharges to air and sea, consumption of chemicals and injected volume. The measurements and calculations shall be performed so that they are representative and the uncertainty is as low as possible"*. The data include methane and nmVOC released during production, transport, and storage of hydrocarbons. The Norwegian Environment Agency compiles and publishes annual reports on greenhouse gas emissions, which include methane and nmVOC data from offshore operations. The emission data is also included in Equinor's Sustainability reporting.

More accurate reporting methods for emissions are essential for protecting the environment, public health, and Equinor's long-term sustainability. They serve as the foundation for informed decision-making, effective policy development, and responsible business practices in a world increasingly focused on environmental concerns and climate change mitigation.

The currently used method for cold flare emission reporting from produced water is based on total produced water volumes multiplied by a gas solubility constant. The value of the solubility constant and the composition of the cold flare gas is typically based on experience data. The method for calculation of VOC emissions is given in Handbook for quantifying direct methane and NMVOC emissions [6]:

$$U_{CH4} = f_{CH4} \times V_{pw} \times \Delta P \times 10^{-6}\ NMVOC \tag{1}$$

$$U_{NMVOC} = f_{NMVOC} \times V_{pw} \times \Delta P \times 10^{-6}\ NMVOC \tag{2}$$

Where the parameters are from **Table 1**. The produced water quantity V_{PW} is the quantity which passes the degassing point.

Table 1 Terms in the equation for calculating direct emissions [6].

Term	Unit	Explanation
U_{CH4}	tonnes	Methane emissions from produced water in the reporting period
U_{NMVOC}	tonnes	NMVOC emissions from produced water in the reporting period
f_{CH4}	**14** g/m³/bar	Emission factor for CH_4. Grams methane per m³ produced water through the degassing point and per bar pressure drop from nearest upstream degassing point
F_{NMVOC}	**3.5** g/m³/bar	Emission factor for NMVOC. Grams NMVOC per m³ produced water through the degassing point and per bar pressure drop from nearest upstream degassing point*
V_{PW}	m³	Accumulated quantity of produced water through the degassification point during the reporting period
Δp	bar	Operating pressure difference between degassing point and closest upstream degassing point
t	hours	Number of operating hours in the reporting period

*If the pressure and the temperature of the produced water indicate the use of other factors according to [Ref. 1], the operator is free to choose this if relevant documentation is available.

The conventional method is not able to estimate effects of changes in process conditions such as salinity of the produced water and composition of the oil and gas. The method does not consider the composition of the emitted gas. All emissions are reported as methane and nmVOC. In most real field cases a significant fraction of the vent gas can be other components such as CO_2 and water vapour. These identified weaknesses have been the motivation for developing the live automated process simulator for emission reporting from offshore process plants.

4 DESCRIPTION OF THE PRODUCED WATER DEGASSING PROCESS AT GUDRUN

A scheme of the produced water degassing process at Gudrun is shown in Fig. 1. Initially, well streams arrive as a three-phase mixture containing gas, hydrocarbon phase, and aqueous phase with around 10-11 wt% of salts, mostly sodium chloride (NaCl). These phases undergo separation within the two three-phase separators: the first stage and test separator. Subsequently, the produced water proceeds through hydrocyclones to the water degasser where pressure is reduced to 3-5 barg. Hydrocyclones were omitted from the model because their primary function is the separation of oil and water phases, and this equipment is not designed for extracting gas from water.

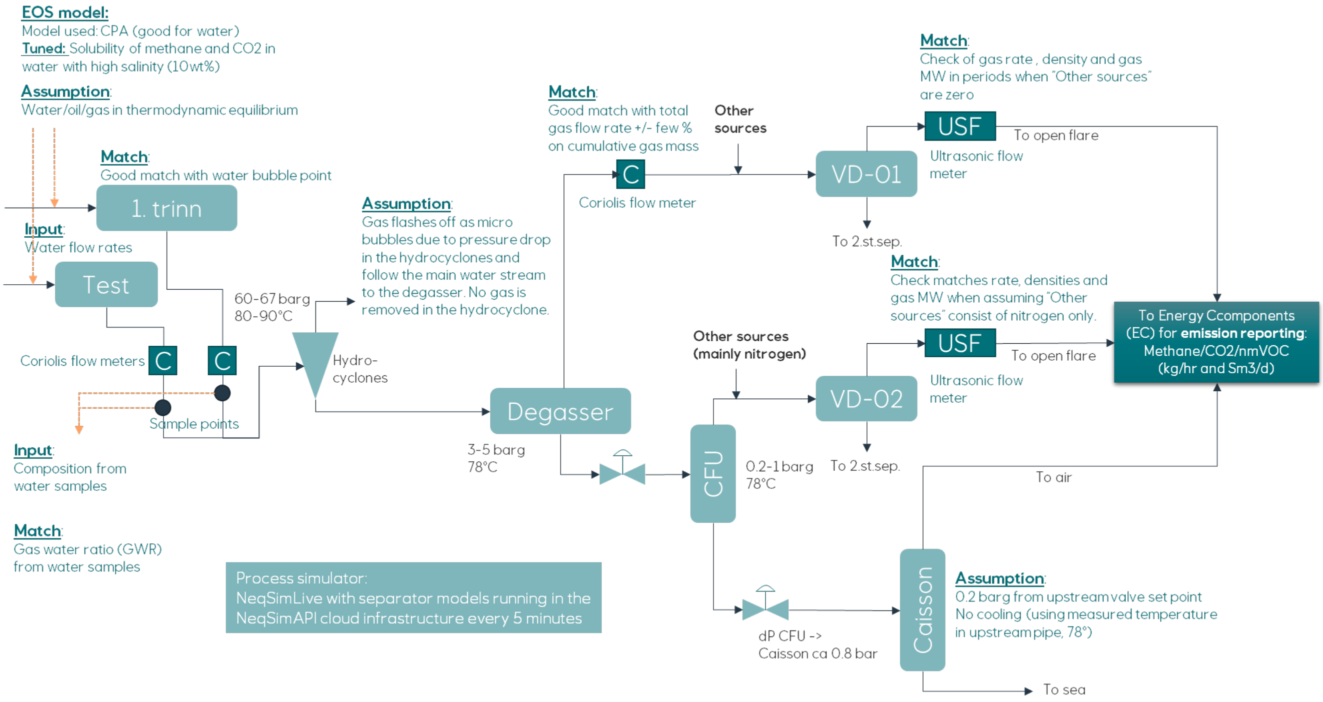


Fig. 1 – Simplified process flow diagram.

Water undergoes further treatment in the Compact Flotation Unit (CFU) downstream the degasser. The CFU serves as an equipment in the water purification process specifically designed to target residual gas when pressure is reduced to 0.2-1 barg. Water at atmospheric pressure is then directed to the caisson before discharge to the sea. Note that temperature throughout the process varies between 90 to 75 °C and the water degasser process is mainly driven by pressure reduction.

Hence, there are three distinct emission sources to air from the produced water degassing process: the gas stream from the degasser, the CFU, and the caisson. The two separate streams, one following the degasser and another from the CFU, are directed to the two separators operating at atmospheric pressure (separators

VD01 and VD02). These streams are combined with emissions from other sources before they are vented to the atmosphere.

There are ultrasonic flow meters installed downstream VD01 and VD02 separators. These flow meters provide the measurements of mass and volumetric flow rates, gas density and molecular weight. However, some deviations between the model and these measurements might occur due to the presence of other emission sources, see section 6.1. Additionally, one can see by comparing the model and measurements, that a constant stream, most likely consisting primarily of nitrogen, is directed towards the separator VD02.

Fig. 1 also shows the Coriolis flow measurements used in the model, water flow rate measurements from the first stage and test separators (as input to the model), and the gas flow rate measurement from the degasser (used for model validation).

Another set of measurements involve water samples from both separators: the first stage and the test separator. These water samples are depressurized to atmospheric pressure and cooled to 15 °C. The gas flashed from water is analysed to determine its composition and the GWR. These measurements serve both as valuable inputs for tuning (gas composition) and validating model predictions (GWR) (see **Table 5** for results). The NeqSimLive model uses constant composition tuned to obtain the correct GWR. The composition is planned updated when a new water sample is available. Normal period between two water samples is six months.

The process was modeled using the NeqSimLive tool. The core of the model fluid description is the Cubic-Plus-Association Equation of State (CPA-EoS) specially developed to improve characterization of complex mixtures containing water, hydrocarbons, and CO_2. See Appendix A for a more comprehensive insight into CPA-EoS used in the model.

5 NEQSIMLIVE FOR EMISSION REPORTING

Running an online process model like NeqSimLive requires a robust and versatile digital infrastructure. Equinor has developed NeqSimLive, running in the cloud based API NeqSimAPI. NeqSimAPI is a process simulator interface running on the Microsoft Azure cloud platform. The NeqSimAPI currently contains 10 process models on eight Equinor facilities, including two test rigs at Equinor Research Centre in Trondheim, Norway. NeqSimLive receives live process data as required for model inputs, runs the models at defined time intervals and writes back simulated variables as tags into Osisoft PI or Aspen for trending and online monitoring. Typically, the process models are run at 5 to 15 minutes intervals.

The connector between NeqSimAPI and PI/Aspen is SIGMA, an Equinor implemented calculation scheduler and interface tool (OPC server). The data flow is illustrated in Fig. 2.

The model purposes vary from online simulation of oil and gas processing, gas dehydration by TEG, produced water emissions, to export gas quality monitoring and estimation of liquid carry-over from scrubbers. The application covered in this article is gas emissions from produced water, and the data flow therefore supports emission reporting to authorities.

Implementing a NeqSimAPI model for a field application requires multidiscipline competence, as shown in Fig. 3. NeqSimLive is the combination of a calculation scheduler (RestAPI consumer/SIGMA) and the NeqSimAPI providing process calculations as a service.

The NeqSim process model itself is implemented in Java and can also be used in alternative frameworks such as Python and .NET [7]. NeqSim includes process unit operations such as separators, compressors, and heat exchangers. The NeqSim library is an open-source library and is called directly from NeqSimAPI. This implementation therefore requires both process and programming competence. Usually, a process engineer codes the process model, which requires insights into the process facility. Close dialog with operations is required.

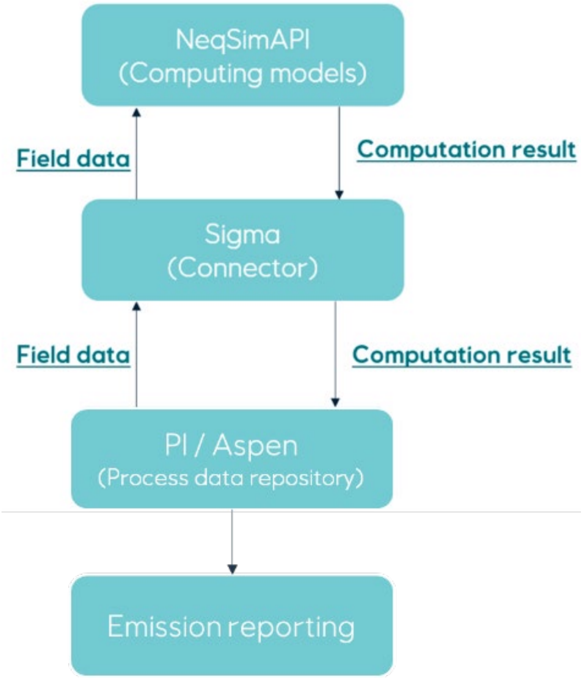


Fig. 2 – Data flow

When the model is up and running, configuration of input and output data is done in SIGMA (Equinor proprietary implementation). In SIGMA, two environments are available, one test environment and one production environment. The process engineer co-operates with IT to obtain a stable operation on the test environment before starting or modifying the production environment. All NeqSimAPI models operate independently. The key success factor is close collaboration between the process and IT disciplines.

For the current application, a third API has been established between PI/Aspen and Energy Components (EC). In EC, daily, monthly and annual values are stored, and data is transferred from EC to Emisoft, which is the portal for emission reporting to the Environmental Authorities, and to MPRML (Monthly Production Reporting Markup Language) for the tax reporting to NPD. This has historically been a manual process, whereas the NeqSimLive implementation enables automation of the emission data reporting.

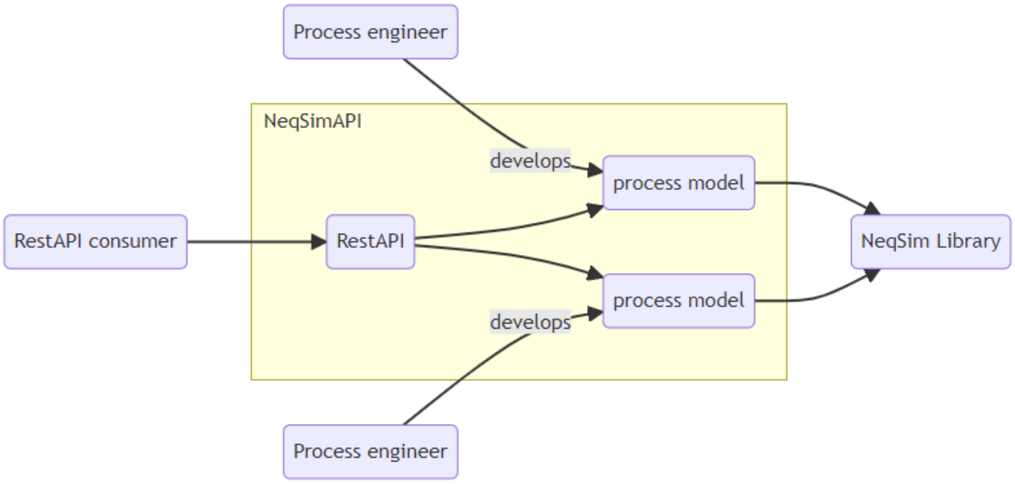


Fig. 3 – The cloud based NeqSimAPI is the heart of the NeqSimLive tool. Process engineers implements new models and a RestAPI consumer schedules calculations at defined intervals.

6 VALIDATION

6.1 Comparison with Field Data

The measured produced water composition and flow rate are used as model input, and the model then provides separate mass flow rates for methane, CO_2 and nmVOC. The simulations predict the gas rate from the degasser and follows the variations and thus gas emissions very well in the entire three and a half year time span that has been investigated (Fig. 4 and Fig. 5). The simulations predict a small, but systematic under-prediction for 2022 and 2023. See section 6.3 for a discussion on model uncertainty.

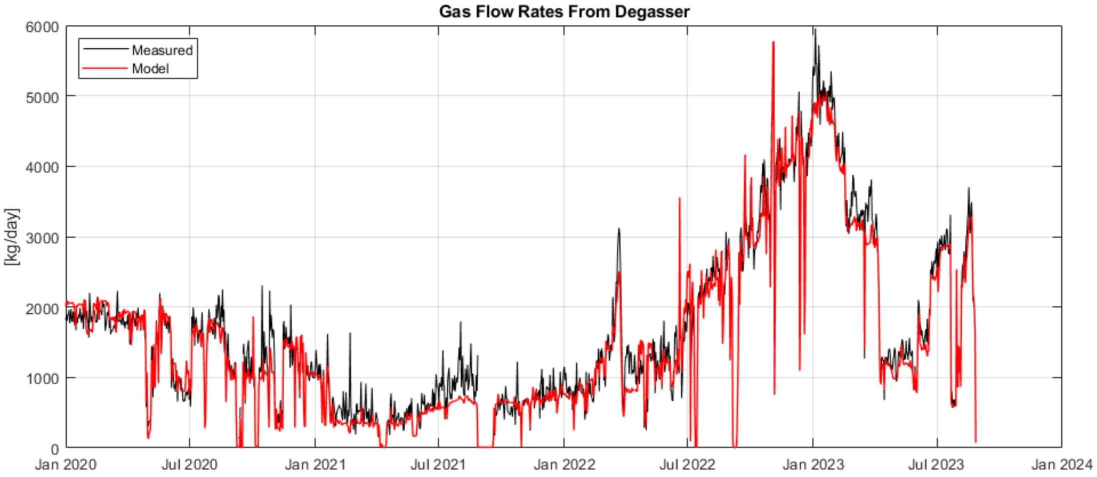


Fig. 4 – Gas flow rate from produced water degasser, comparison between measured (Coriolis) and calculated (NeqSim).

In Fig. 5, the variations in production rates are shown, and the corresponding component flow rates from the simulations.

The simulations have been validated by comparing simulated GWR and compositions with water samples. An uncertainty assessment is presented in Appendix B. In **Table 5** (Appendix B) the simulations of the first stage separator reproduce the GWR with a deviation from -1 to +4% deviation from water sample analysis GWR values. The model was tuned on GWR on the water sample taken in January 2023. The reproduction is equally good for the entire time range from January 2020 to August 2023. The GWR has varied from 1.15 to 1.43 Sm^3/Sm^3, and the model has captured these variations. The model captures CO_2 fraction during 2022 and 2023 but is not able to capture the lower CO_2 content equally well in the 2020 sample.

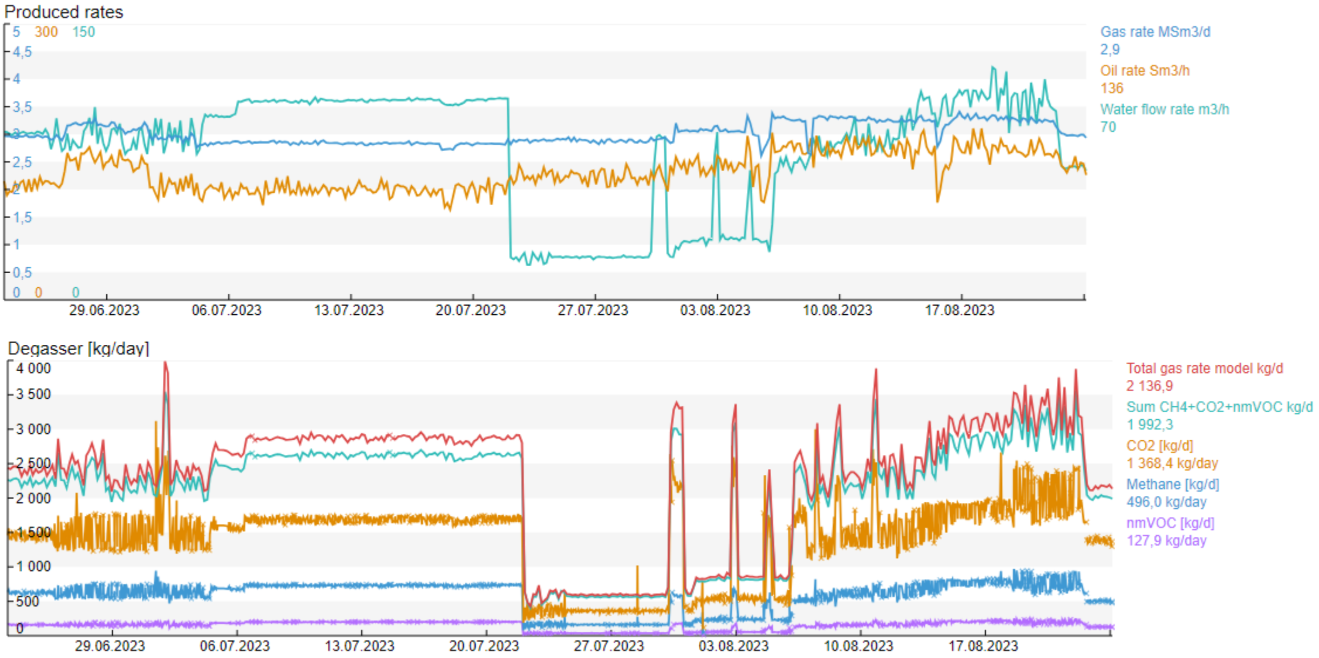


Fig. 5 – Trending of model predicted CO_2, methane and nmVOC flow rates. Screenshots from PIVision user interface.

For nmVOC, the discrepancy is higher. This is mainly an effect of the small amounts of these components, where also the uncertainty in the laboratory analyses becomes significant.

The test separator 2023 composition used in the tuning gives high deviations when comparing against 2020 water sample composition. This is believed to be because the 2023 sample was taken from a mixture of two wells, while the 2020 sample was from only one.

The model uses a fixed produced water composition as input to process calculations (see section 4). The results suggest that the model should be re-tuned when the well stream composition changes. Current procedure is to take produced water samples two times each year, which seems to be a reasonable tuning frequency unless CO_2-rich wells or wells with significant change in composition or salinity are started or shut down.

An ultrasonic flow meter is installed downstream separator VD01, in series with the Coriolis on the degasser. Comparison with gas mass flow rate, gas density and molar mass shows equally good performance (Fig. 6).

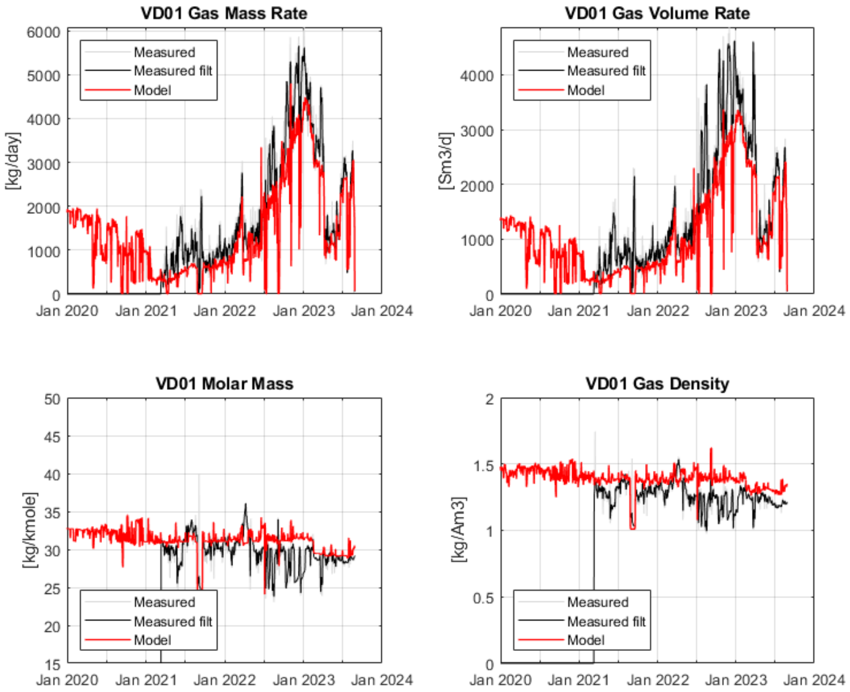


Fig. 6 – Gas flow rate, density and molar mass, comparison between ultrasonic meter readings and model predictions for flare knock-out drum VD01. Note that the flow meters were installed in January 2021.

Comparison of simulated and measured gas flow rate from the CFU shows a significant underestimation in the model predictions (Fig. 7). This is believed to be due to "other gas sources" upstream separator VD02. As seen in Fig. 8, gas flow is measured during periods with no produced water. On average, 25 kg/hr (600 kg/day) gas mass flow rate is measured during these periods. Most of the time, this rate corresponds well with the offset in gas mass rate between measured and simulated for VD02 (Fig. 7).

It may be assumed that this gas stream *most of the time* is nitrogen from utility gas systems. This assumption has been tested by comparing simulated gas molar mass with molar mass measured by the ultrasonic flow meter. If not adjusting for a nitrogen stream, the simulated molar mass is about 40 g/mole, while the measured is just below 30 g/mole (Fig. 9). With this adjustment the simulated molar mass also becomes 30 g/mole, indicating that the assumption is reasonable.

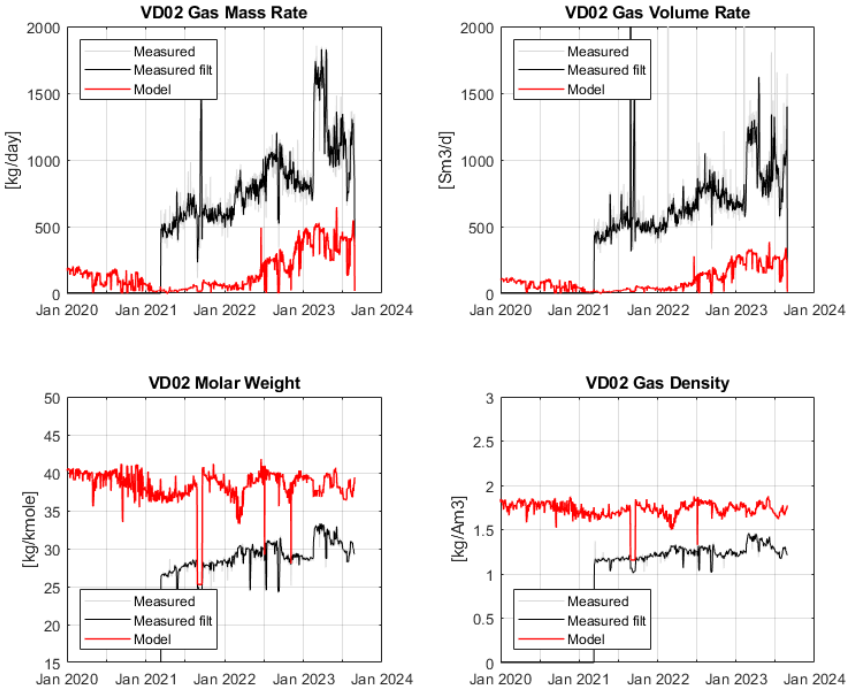


Fig. 7 – Gas flow rate, density and molar mass, comparison between ultrasonic meter readings and model predictions for flare knock-out drum VD02. The large discrepancy is attributed to inflow from other sources, mainly nitrogen. Note that the flow meters were installed in January 2021.

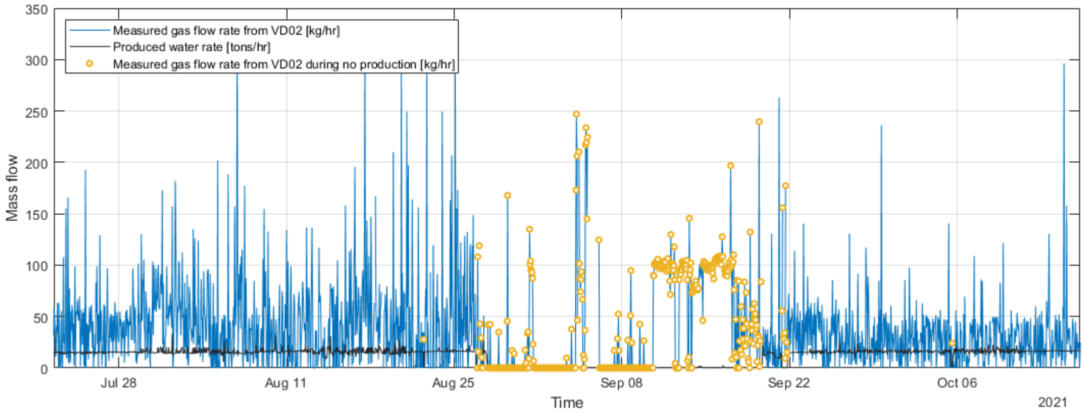
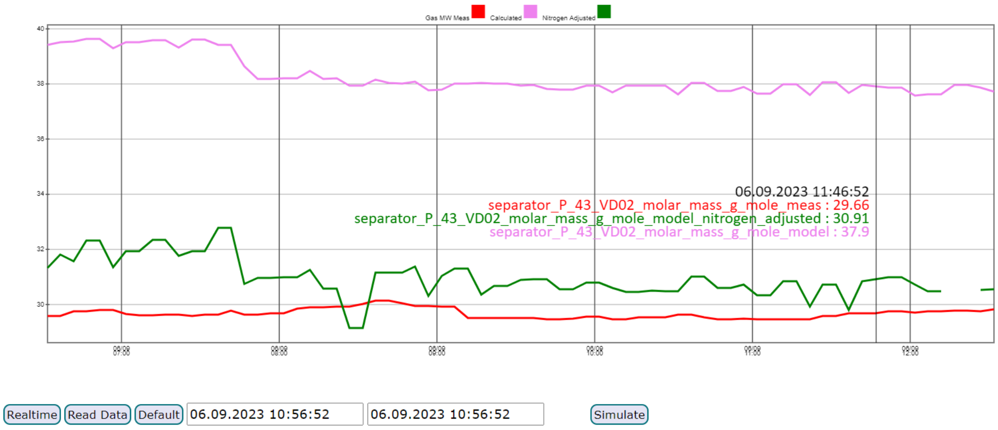


Fig. 8 – Mass flow rate measured on the gas outlet of VD02 during periods with no produced water flow (average value 25 kg/hr gas mass flow during these periods).



```
06.09.2023 11:46:52
separator_P_43_VD02_molar_mass_g_mole_meas : 29.66
separator_P_43_VD02_molar_mass_g_mole_model_nitrogen_adjusted : 30.91
separator_P_43_VD02_molar_mass_g_mole_model : 37.9
```

06.09.2023 10:56:52
06.09.2023 10:56:52

Fig. 9 – Calculated molar mass measured by Ultrasonic flow meter and NeqSim calculation on gas stream from knock-out drum VD02. The green molar mass line represents simulated molar mass when assuming gas entering from "other gas sources" consists of Nitrogen. Screen dumps from SIGMA.

6.2 Comparison with Conventional Approach

Constant factors for gas solubility in water, expressed as g/m³/bar (see **Table 1**, and Eq. 1 and 2), introduce significant inaccuracy in emission reporting. This approach tends to result in much less precise predictions, especially when conditions differ from the reference conditions.

Also, these factors are quite conservative. The model predicts 5-6 g/m^3/bar for methane and 1.2-1.4 g/m^3/bar for nmVOC (see Fig. 10 and Fig. 11), which is 60% lower than the factors used in the conventional method. The simulation model predicts 15 to 30 g/m^3/bar for CO_2 (Fig. 12).

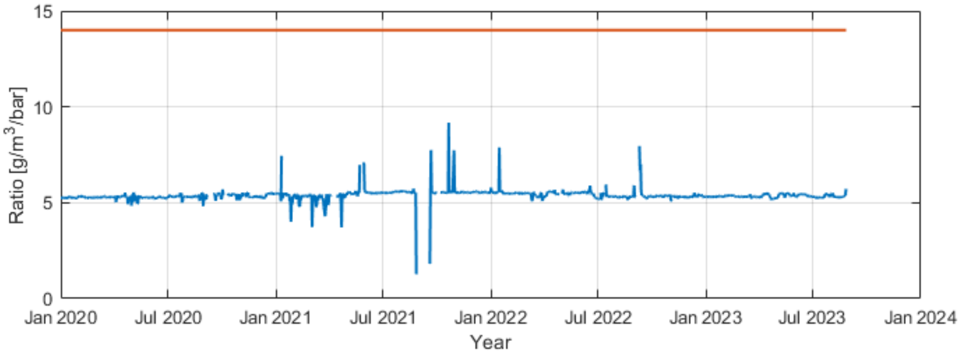


Fig. 10 – Factor for methane predicted by the model. The conventional method uses 14 g/m^3/bar [6].

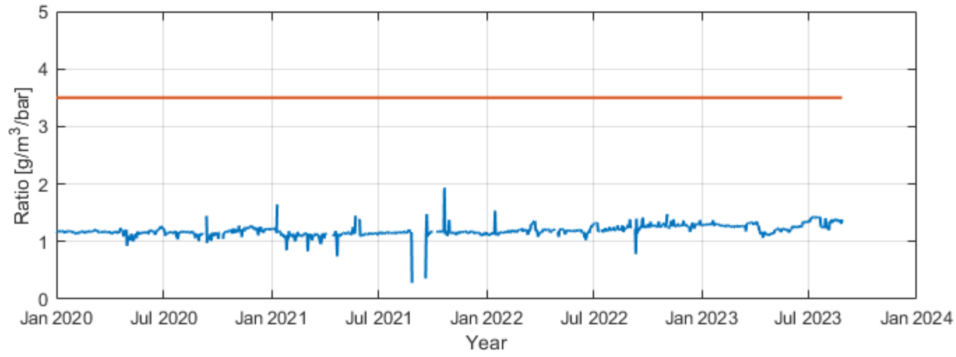


Fig. 11 – Factor for nmVOC predicted by the model. The conventional method uses 3.5 g/m³/bar [6].

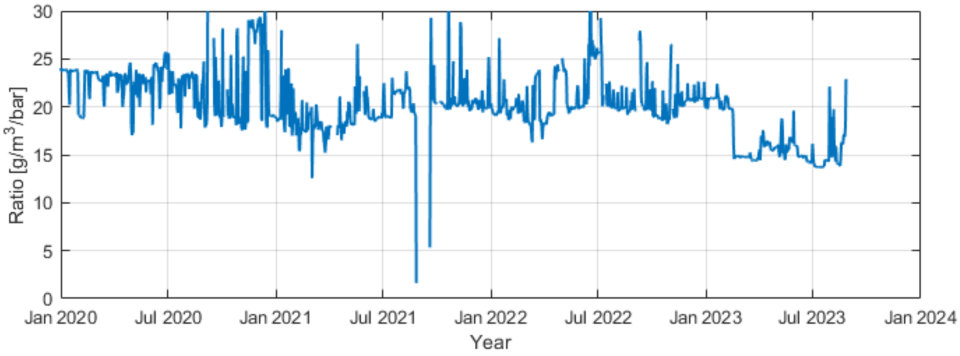


Fig. 12 – Factor for CO_2 predicted by the model. The conventional method does not report carbon dioxide [6].

6.3 Method Uncertainty

The absolute and relative uncertainties have been estimated by two methods. The first method is to compare calculated gas rate with measured gas rate and molar mass. The second method, described in Appendix B, estimates mass flow rate uncertainty per component and total gas from the uncertainties of the model inputs. Comparison with annual cumulative gas mass is shown in Fig. 13. The model was tuned with water samples taken January 16th, 2023.

The first uncertainty estimation method is shown in right plot in Fig. 13, showing cumulative relative discrepancy between measured and simulated total gas rates from the degasser. The cumulative, annual discrepancy was +3% at end of 2020, -20% end of 2021, -2.0% at the end of 2022, and -7.2% at the end of first half of 2023. The large discrepancy in 2021 may be attributed to the low absolute rate, since the Coriolis gas flow meter has higher uncertainty at low rates, and this uncertainty accumulate over time. This is indicated in the cumulative graph. This comparison shows that for the current process, one tuning water sample can be used to simulate a long-time span, and within the uncertainty requirements of ±7.5% [6].

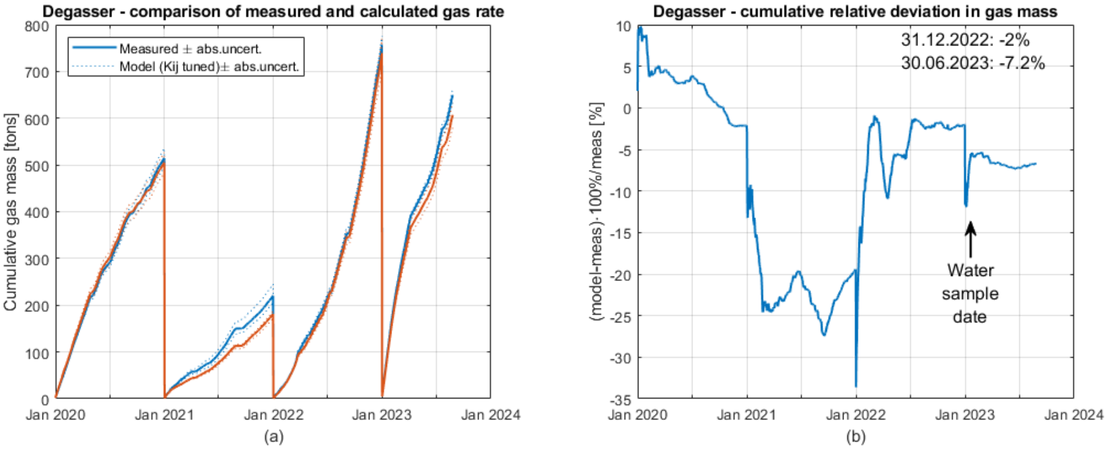


Fig. 13 – Cumulative gas emissions from the produced water degasser (a) and relative deviation between measured and simulated gas rate (b).

The second method is shown in Appendix B and considers how gas streams are calculated and the uncertainties in the model's input variables. This is a complex method that has been simplified in this work but is believed to give a good representation of the uncertainties for the mass streams of CO_2, methane, nmVOC and total gas emissions. The uncertainty for total, simulated gas mass rate is shown as the error bands in the left hand plot in Fig. 13. The average uncertainties over the investigated period are shown in **Table 4**, and on average for 2022 and 2023:

CO_2:	±3.6%	nmVOC:	±38%
Methane:	±7.4%	Total gas rate:	±3.6%

The first method will be used for online monitoring of the model, while the second method is used for validating the method.

7 EMISSION REPORTING – NEW METHOD

CO_2, methane and nmVOC flow rates are stored in 5 minutes intervals in PI, the facility's data storage system. Pressures and temperatures are relatively constant in the degassing part of the process. In section 6.1, it is shown how the model captures the varying process conditions with respect to flow rates. Using the new method, insights can be gained from the highly non-steady flows and day-to-day decisions can over time reduce emissions.

Modelled accumulated annual emissions for CO_2, methane and nmVOC are shown in Fig. 14, showing the high content of CO_2 not currently captured by the conventional emission reporting method. The new method shows that during the past four years, about 72-78 wt% of the emissions currently reported as methane and nmVOC, is CO_2.

Fig. 15 outlines the difference in emission reporting and CO_2-equivalents by using the conventional method (Eq. 1 and 2) and the NeqSimLive method. In 2022, the reported emissions using the conventional method were 11 000 CO_2 equivalents. The conventional method reports methane and nmVOC only and does not report CO_2 emissions. NeqSimLive calculates emissions also for CO_2. NeqSimLive calculates much lower hydrocarbon (methane and nmVOC) emissions, but higher total emissions due to inclusion of CO_2. Methane and nmVOC have higher environmental impact than CO_2, with CO_2 equivalent factors of 28 and 2.2 respectively. In sum, the new method reduces the reported CO_2 equivalent emissions by 58%, to about 4 700.

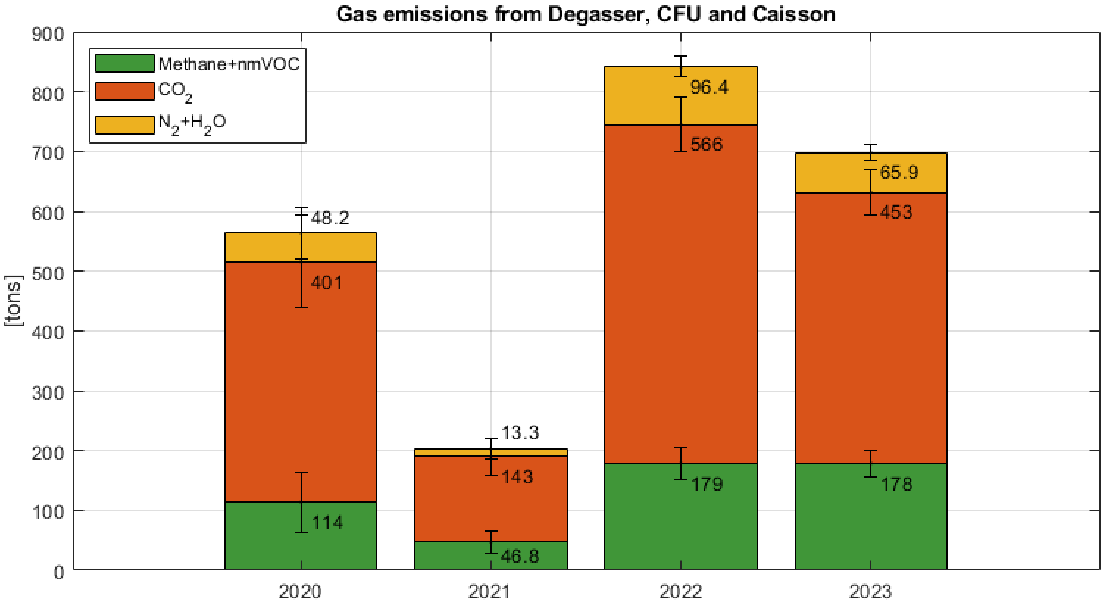


Fig. 14 – NeqSimLive predictions of annual gas emissions from produced water. The error bars show the estimated model uncertainty per component.

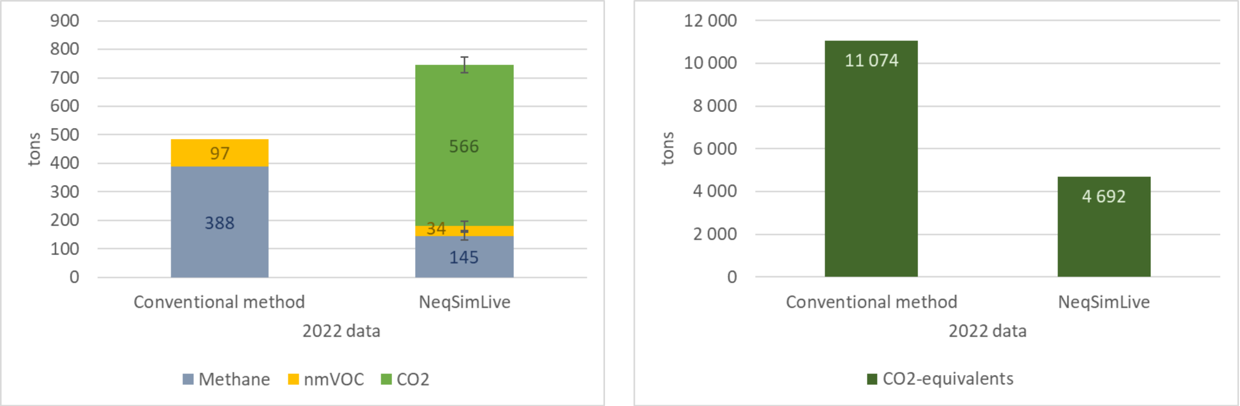


Fig. 15 - Emissions from produced water, comparison of conventional method (Eq. 1 and 2) and NeqSimLive method. The error bars show the estimated model uncertainty per component.

8 CONCLUSIONS

A virtual measurement method using an online process simulator (NeqSimLive) has been implemented for online calculation of greenhouse gas emissions from Gudrun. The objective is to provide accurate emission reporting for methane, nmVOC and CO_2 released to air though the cold flare.

Previous reporting method uses constant and average solubility factors for methane and nmVOC and assumes all emissions are hydrocarbons. The new method provides virtual measurements of CO_2 emissions, in addition to methane and nmVOC emissions.

The new emission reporting method shows that ¾ of the emissions are CO_2, and Gudrun emission numbers for 2022 can be reduced from 11 000 to 4 700 CO_2 equivalents.

The new method has an estimated uncertainty of GWR, gas and CO_2 emissions of ±4%, which is within the authority requirement of ±7.5% for emission gases. It is more accurate than the conventional reporting method. NeqSimLive captures solubility effects of salinity of water, well stream composition and variations in process pressure and temperature.

Periodic calibration is required. It is difficult to recommend a specific calibration interval, as it is dependent on how much the well stream composition varies. The currently available water analyses data at Gudrun suggest that two water samples per year is sufficient if the well compositions are constant. For Gudrun, back production of injection freshwater is expected soon, and this will affect water salinity and thus the gas solubility. Such an event will require a new calibration, both with gas composition and water salinity.

The NeqSim library has accurate models for glycol-based dehydration processes, including hydrocarbon losses from such processes. The technology presented in this paper can be used to estimate methane and VOC emissions from glycol dehydration with improved accuracy compared to the methods used today.

NeqSim is an open-source process simulation package and can freely be used in third party applications. Implementing NeqSim via a cloud solution such as has been done in NeqSimLive, makes the solution scalable and fit for use in new digital solutions such as online process simulation and digital twin technologies.

9 NOTATION

gmf	[kg/kg]	Gas-Mass-fraction
GWMF	[kg/m^3]	Gas to water mass factor
GWR	[Sm^3/Sm^3]	Gas-Water-Ratio
nmVOC		Non-methane volatile oil components
NeqSim		Open-souce (non-equilibrium) process model
NeqSimLive		Online running process model implementation of NeqSim for a specific facility
NeqSimAPI		Digital framework for running and accessing a NeqSimLive model

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APPENDIX A – CPA EoS Fluid Model

The Cubic-Plus-Association Equation of State (CPA-EoS) has been developed to improve classic equations of state to better represent mixtures of hydrocarbons and polar components. The model has been successfully applied to mixtures containing diverse components like water, carbon dioxide, hydrocarbons, alcohols and glycols. CPA combines the SRK equation with an association term from the Wertheim theory. In cases where no associating compounds are present, the CPA equation reduces to the Soave-Redlich-Kwong (SRK) equation of state [3]. The CPA-EoS is expressed as

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - 0.5\left(\frac{RT}{V_m}\right)\left(1 + \frac{1}{V_m}\frac{\partial lng}{\partial\left(\frac{1}{V_m}\right)}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \tag{3}$$

where V_m is the molar volume, X_{A_i} is the fraction of A-sites of molecule i that are not bonded with other active sites, and x_i is the mole fraction of component i. The letters i and j are used to index the molecules, whereas the letters A and B indicate the bonding sites on a given molecule.

The mixing and combining rules for a and b are the classical van der Waals one-fluid rules. For the coefficient a the formula is the following:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{4}$$

where the often used combining rule:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{5}$$

where $\mathrm{k_{ij}}$ is the binary interaction parameter. The binary interaction parameters are calculated as function of temperature in Kelvin.

$$k_{ij} = k_{ij,0} + k_{ij,T}(T - 288.15) \tag{6}$$

Binary interaction parameters help adjust the predictions of the model to better match the real-world behaviour of the mixture. These parameters are specific to the pair of components being considered and reflect the extent to which their interactions deviate from ideal behaviour.

Considering that Gudrun produced water has 10–11 wt% of NaCl, our strategy involves employing the CPA model with updated binary interaction parameters.

Modelling the solubility of gases in the presence of a substantial concentration of salts in water is challenging, and the challenge lies in accurately capturing salt-induced solubility changes. By refining model parameters to reflect the influence of salts, the purpose is to attain precise hydrocarbons and CO_2 solubility in water. An illustrative instance of this can be drawn from the work of Søreide and Whitson [1]. They successfully made changes to the PR equation of state to account for the influence of salinity in the aqueous phase. The solubility of natural gas with varying NaCl brine salinity showed good agreement between measured data in a wide range of pressures and temperatures.

The water sample 2023-00539 (see **Table 5**) was used for the model tuning to obtain the following binary interaction parameters, **Table 2**:

Table 2 Tuned binary interaction parameters for saline water.

	Binary Interaction Parameters	
	$k_{ij,0}$	**$k_{ij,T}$**
CO2	-0.24	0.001121
Methane	-0.72	0.002605
Ethane	0.11	0
Propane	0.205	0
i-Butane	0.081	0
n-Butane	0.17	0

These parameters played an important role in improving the predicted solubility and enabled us to accurately represent the parameters of the water sample. Water samples from the Gudrun field obtained from the first stage and test separators provide parameters for tuning such as the gas composition [mole fraction] and GWR at standard conditions (see **Table 5**). **Table 3** presents a comparison of the model predictions after tuning these parameters:

Table 3 Comparison of model predictions to lab data of water sample.

	Lab Data	**Tuned model**
GWR	1.22	1.24
CO_2	50.97	50.92
Methane	43.73	43.98
Ethane	3.72	3.72
Propane	1.02	0.96
i-Butane	0.08	0.07
n-Butane	0.17	0.14

With these updated parameters in place, we are now able to compare the findings with existing literature data. It is important to note that the model has been tuned using a water sample with an approximate salinity of 10–11 wt% or 1.7–1.9 mole of NaCl per litre. As a result, the model predictions should correspond to this salinity level when compared to the data available in the literature. As one can see, the model placement aligns well with the expected values (see Fig. 16, Fig. 17 and Fig. 18).

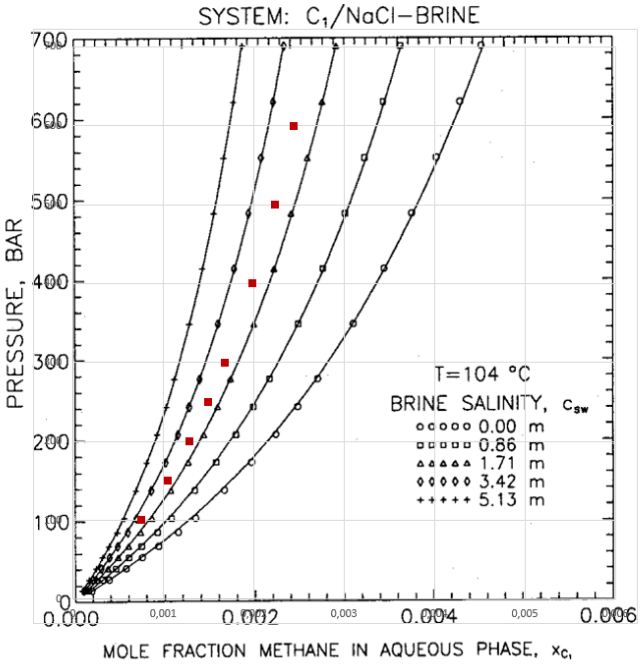

Fig. 16 – Comparison of experimental solubility and model (red points) for methane [1].

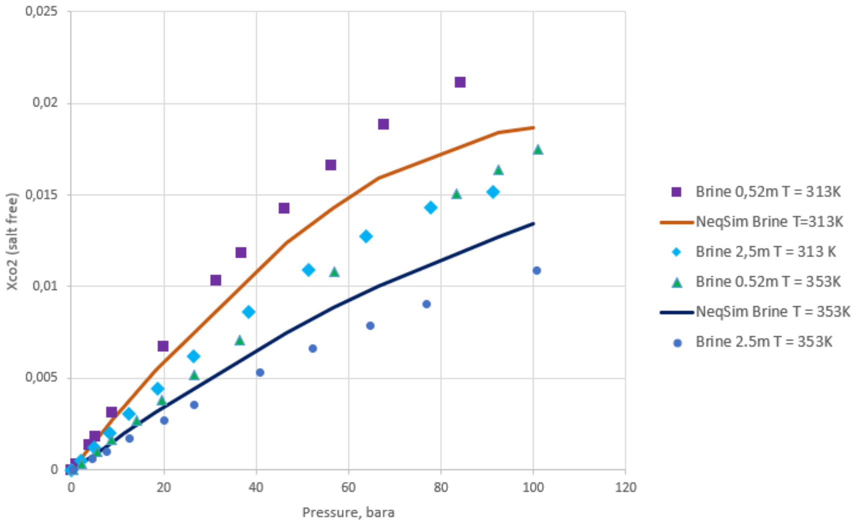

Fig. 17 – Validation of the predictive capability of the updated model using experimental data [4] for CO_2 solubility in the system $CO_2 + H_2O + NaCl$.

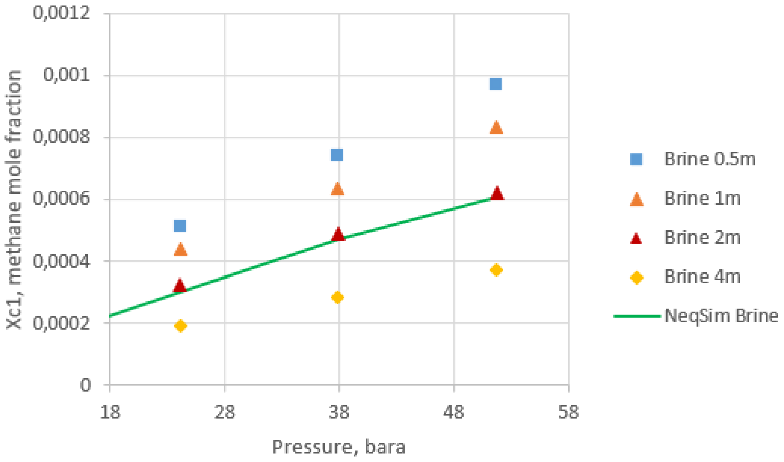

Fig. 18 – Validation of the predictive capability of the updated model using experimental data [5] for methane solubility in the system $CH_4 + H_2O + NaCl$ at T = 298 K.

APPENDIX B – MODEL UNCERTAINTY

The following method has been used to estimate the uncertainties in simulated gas flow rates, both total gas rates and component rates. The gas flow rate is modelled as:

$$m_g = m_w \cdot gmf \tag{7}$$

where

m_g is the simulated gas mass flow rate [kg/hr]
m_w is the measured water flow rate from the inlet and test separators [kg/hr]
gmf is the simulated gas mass fraction [-]

The mass flow $m_{g,i}$ [kg/hr] for component i is then:

$$m_i = m_g \cdot y_i = m_w \cdot gmf \cdot y_i \tag{8}$$

where

y_i is the calculated mass fraction of component i [-]

The absolute uncertainty in the gas mass flow rate is then modelled as:

$$\begin{aligned}\Delta m_g &= \pm\sqrt{\left(\Delta m_w \cdot \frac{\partial m_g}{\partial m_w}\right)^2 + \left(\Delta gmf \cdot \frac{\partial m_g}{\partial gmf}\right)^2} \\ &= \pm\sqrt{(\Delta m_w \cdot gmf)^2 + (\Delta gmf \cdot m_w)^2}\ \text{[kg/hr]}\end{aligned} \tag{9}$$

where

Δm_w is the flow rate uncertainty from the water flow meters (Coriolis) [kg/hr]
Δgmf is the estimated uncertainty in the gas mass fraction [-]

Estimating Δgmf is challenging, gas mass fraction will vary with pressure, temperature, and composition. It has been assumed that the relative uncertainty in gmf is proportional to the relative deviation in GWR:

$$\Delta gmf = gmf \cdot \frac{\Delta GWR}{100\%} = \frac{m_g}{m_w} \cdot \frac{\Delta GWR}{100\%} \tag{10}$$

A sensitivity analysis has been performed to estimate ΔGWR (Appendix C).

For each component i the flow rate uncertainty then becomes:

$$\begin{aligned}\Delta m_i &= \pm\sqrt{\left(\Delta m_w \cdot \frac{\partial m_i}{\partial m_w}\right)^2 + \left(\Delta gmf \cdot \frac{\partial m_i}{\partial gmf}\right)^2 + \left(\Delta y_i \cdot \frac{\partial m_i}{\partial y_i}\right)^2} \\ &= \pm\sqrt{(\Delta m_w \cdot gmf \cdot y_i)^2 + (\Delta gmf \cdot m_w \cdot y_i)^2 + (\Delta y_i \cdot m_w \cdot gmf)^2}\end{aligned} \tag{11}$$

where

Δy_i is the abs. mass fraction uncertainty from the water sample analysis [-]. This report uses the uncertainties in the water sample from January 2023 for the entire calculated period.

The uncertainties in calculated gas and CO_2 emissions seem reasonable when compared to the uncertainty in the reference gas meter readings, see **Table 4**. See also direct comparison with measured gas rate in Fig. 4 estimated error bands in cumulative values, Fig. 14.

Table 4 Relative uncertainty for mass flow rates modelled by NeqSimLive

Year	CO_2	Methane	nmVOC	Total gas rate
2020	12.0%	23.4%	53.7%	9.8%
2021	12.3%	23.3%	49.6%	10.1%
2022	3.4%	7.5%	48.6%	3.5%
2023	3.7%	7.2%	38.4%	3.7%

Table 5 Comparison of Compositions from water samples and NeqSim predictions. Upper table is from first stage separator, the lower table is from the test separator. Sample data are averages of three water samples taken on the same date.

1. stage separator	Water samp.	NeqSim	Dev.	Water samp.	NeqSim	Dev.	Water samp.	NeqSim	Dev.
	average*	calc		average	calc		average	calc	
Sample date:	16.01.2023	16.01.2023		29.06.2023	29.06.2023		17.04.2020	17.04.2020	
GWR	1.22	1.24	-1 %	1.17	1.13	4 %	1.43	1.45	-1 %
CO2	50.97	50.92	0 %	51.53	51.68	0 %	47.57	53.08	-12 %
Methane	43.73	43.98	-1 %	43.11	43.57	-1 %	47.00	42.72	9 %
Ethane	3.72	3.72	0 %	3.82	3.50	8 %	3.94	3.17	20 %
Propane	1.02	0.96	6 %	1.06	0.86	19 %	1.04	0.73	29 %
i-Butane	0.08	0.07	9 %	0.07	0.06	14 %	0.06	0.05	17 %
n-Butane	0.17	0.14	18 %	0.17	0.12	29 %	0.19	0.10	47 %
nmVOC	5.29	5.10	4 %	5.37	4.75	11 %	5.43	4.20	23 %

** One of three samples were used for model tuning of GWR*

Test separator*	Water samp.	NeqSim	Dev.	Water samp.	NeqSim	Dev.
	average	calc		average	calc	
Sample date:	16.01.2023	16.01.2023		17.04.2020	17.04.2020	0
GWR	1.75	1.72	2 %	1.15	0.63	45 %
CO2	66.18	65.47	1 %	44.98	59.40	-32 %
Methane	29.05	31.00	-7 %	48.09	35.74	26 %
Ethane	2.97	2.60	13 %	4.28	3.41	20 %
Propane	0.85	0.67	21 %	1.26	0.99	22 %
i-Butane	0.06	0.05	17 %	0.21	0.08	61 %
n-Butane	0.18	0.10	43 %	0.88	0.17	80 %
nmVOC	4.78	3.53	26 %	6.93	4.86	30 %

** No water samples were taken from the test separator water on 29/6-2023*

APPENDIX C – Sensitivity analysis

Sensitivity analysis is an important aspect of assessing the uncertainty of the proposed simulation method. Five key parameters were considered for evaluation: pressure in the first stage separator, temperature in the first stage separator, CO_2 input fraction to the first stage separator, and the salinity level. However, the model was tuned to maintain a constant salinity level (10-11 wt% NaCl) and for now does not take the salinity as input.

For the selected parameters (pressure, temperature, and CO_2 input fraction) a systematic approach was taken. These parameters were randomly varied within a 5% range. The resulting sensitivity graph provides insight into how deviation in these parameters influence the GWMF at degasser conditions (see Fig. 19).

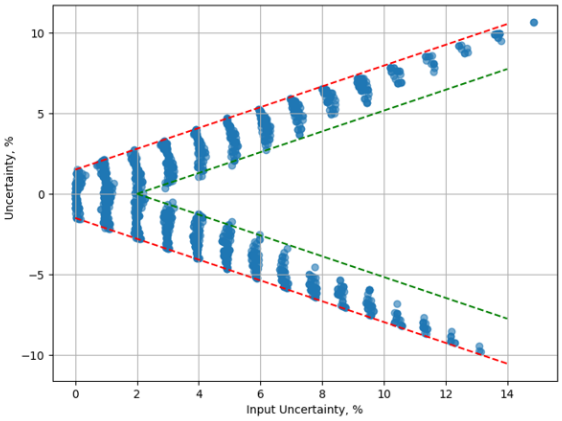

Fig. 19 – Multi-parameter sensitivity analysis of the model: impact of pressure, temperature, and CO_2 input fraction on GWMF change. The red line represents the upper uncertainty limit, while the green line represents the lower uncertainty limit.

Equation 12 combines the uncertainties of pressure, CO_2 input fraction, and temperature into a single parameter (input uncertainty).

$$input_{UNC} = CO_{2_{UNC}} \cdot P_{UNC} \cdot T_{UNC} \tag{12}$$

Assuming 1 % uncertainty for the pressure and temperature input values, and CO2 input fraction uncertainty assuming to be equal to the deviation between measured during water sample and simulated (see **Table 5**), the following GWR uncertainty is achieved, see **Table 6**. GWR uncertainty equals GWMF uncertainty.

Table 6 Relative uncertainty of GWR modelled by NeqSimLive at degasser conditions.

Year	Input Uncertainty, %	GWR Uncertainty, %
2020	14.25 %	10.7 %
2021	14.25 %	10.7 %
2022	2 %	2.8%
2023	2.3 %	3.0%