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MARINTEK REPORT

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VOC - Methane Recovery

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ABSTRACT

Several methods for reduction of VOC and methane emission from the cargo tanks on crude oil carriers have been considered. They have been grouped into operational methods, separation methods and combustion methods.

Combinations of different methods have also been evaluated.

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1. SUMMARY AND CONCLUSIONS

Several methods for reduction of VOC and methane emission from the cargo tanks on crude oil carriers have been considered. They have been grouped into operational methods, separation methods and combustion methods.

Table 1.1 summarizes properties for (some of) the methods evaluated.

Sequential Transfer of Tank Atmospheres gives only small to moderate reduction of methane emission.

Applying HC cover gas will reduce the mass of VOC released from the cargo during loading. But if it is not combined with other measures, the emission of VOC from the cargo tanks to the atmosphere may significantly increase. The emission of methane from the cargo tanks will not be reduced either, but more likely also significantly increased, see Section 3.1.2. The operational characteristics of the additional measure that HC cover gas must be combined with, determines if the emission of methane to the air will become reduced or not.

Removing more light ends from the cargo before loading in order to reduce the vapour pressure of the crude, may significantly reduce both the VOC and the methane emission. But the mass of the extra removed light ends may become 5 to 7 times larger than the reduced mass of VOC emission.

The effect on the methane emission from reduced temperature of the loaded cargo becomes very moderate.

Traditional recovery plants do not reduce the methane emission significantly.

A conclusion is that today there is no commercially available simple recovery processes that will significantly reduce the methane emission for application on a shuttle tanker. A combination of processes will be needed. A combination of a recovery plant and power production from the un-recovered gas seems to be the best alternative. The produced power can either be used to pull a generator or rotating equipment of a recovery plant (direct drive). Both alternatives are included in the term “power production” in this report.

Power production, exhaust as cover gas

The un-recovered gas downstream of a recovery plant is a wide variation of lean low calorific gases depending on e.g. the loaded crude oil and the recovery technique applied. These gas qualities could be fed to a gas engine for power production. Gas engines in the range of 2-4 MW is available (one, two or three units) but have to be adapted to the specific case and improved control system for handling variation in gas qualities. The available gas pressure is ideal for gas engines, see section 3.3.3.3.

A steam turbine plant could be used for power production, but is pr. date not seen as the best solution due to complexity and cost (no references, has to be a tailor made system)

Gas turbines are not feasible to this type of gases and especially the large variation in gas quality.

Power production, hydrocarbons as cover gas

The un-recovered gases in this case are pure hydrocarbon gases with low methane number. These gases can be burned in gas engines that are available in several sizes (one, two or three units). Gas engines have to be de-rated due to the low methane number, and knocking detecting systems will be required. The available gas pressure is ideal for gas engines.

Gas turbines are well suited for these types of gases. But they require a gas booster to raise the pressure from about 10 bar to 20-25 bar. Steam turbines systems can also be tailor made for such applications.

The aspects of safety, rules and regulations must be sorted out before HC cover gas can be applied on a shuttle tanker. However, the fact that it is already used on a FPSO indicates that it is possible to do so.

The inclusion of power production may seem to increase the complexity of the recovery system. But it must be remembered that most of the existing shuttle tankers have too little electric power available for a recovery plant. Additional power generation must therefore be installed on most shuttle tankers, and the preference seems to be a separate and dedicated power pack. This fact has been taken into consideration when the costs of processes combined with power production are evaluated to medium in Table 1.1.

Table 1.1 Summary of basic features for some recovery processes

Method		Recovery/reduction potential		Current Status		Complexity	Power Consumption	Cost
		VOC	Methane	Technical	Commercial			
Exhaust cover gas	Sequential Trans. Tank Atmos.	Moderate	Small	Developed	Available	Low	0	Low
	Removing light ends of cargo before loading	Medium	Medium to high	Developed	Available			High
	Absorption in cargo	Moderate to high	Small	Developed	Available	Medium	Medium	Medium
	Condensation	Moderate to high	Small	Developed	Available	Medium to high	Medium	Medium
	Adsorption and condensation	Moderate to high	Small	Partly developed	Partly available	Medium to high	Medium	Medium to high
	Membrane and condensation	Moderate to high	Small	Need development	Not available	Medium to high		Medium to high
	Hydratization	High	Moderate to high	Need development	Not available	High	Very high	High
	Condensation with cryogenic cooling	High	High	Partly developed	Partly available	High	High	High
	Absorption or condensation with power production	High	High	Almost developed	Almost available	Medium	0	Medium
HC cover gas	Absorption with power production from gas engine	High	High	Need development	Almost available	Medium	0	Medium
	Condensation with power production from gas engine	High	High	Developed	Almost available	Medium	0	Medium

2. PROJECT BASIS

2.1 Objective

The objective of this study is to update the client about the technical and the economical status of VOC recovery methods that are capable of recovering methane. The area of application is mainly crude oil carriers, with particular attention to shuttle tankers.

2.2 Introduction

During year 2000 SFT (the Norwegian Pollution Control Authority) started to regulate the emission of NMVOC (Non-Methane Volatile Organic Compounds) from offshore crude oil storage and loading, by issuing emission permits to the operators on the Norwegian Continental Shelf. The emitted VOC (Volatile Organic Compounds) also contains methane. It is, however, recognised that the reduction of emitted methane is not easy to obtain. This is believed to be the reason why the emission permits only considers NMVOC. Also methane is less active in the formation of smog and ground-near ozone.

The emission of methane contributes to the green house effect, and should therefore also be diminished. Oljeindustriens Landsforening (OLF) has asked MARINTEK to perform a review on the status of possible methods for methane emission reduction. The study has been performed in cooperation between MARINTEK and SINTEF Energy Research A/S.

2.3 Study Basis

The study is mainly based on experience and competence already existing at the SINTEF Group at start of the project.

As far as simulations have been performed, they are to a great extent based on the emission situation existing on the Statfjord field when all cargo tanks on a shuttle tanker is loaded in parallel under mean weather conditions. The loading rate is 8000 m³/h (high loading rate for a shuttle tanker).

The cover gas filled into the cargo tanks during discharge, is traditionally referred to as an inert gas. In most cases, this “inert” gas is really an exhaust gas produced by burning diesel/heavy oil (incinerator). Typical composition is 83 % N₂, 12 % CO₂ and 5 % O₂. The term exhaust gas will be used in this report, because it gives a better description of the gas. If the term inert gas is found, it should be interpreted as exhaust gas. Note that the use of hydrocarbons as cover gas is also a topic in this report.

This report is an overview of several possible methods. The specific recovery methods will therefore not be dealt with in depth.

3. RECOVERY METHODS

The VOC and methane recovery methods considered have been grouped into:

- Operational methods
- Separation methods
- Combustion methods

3.1 Operational Methods

The operational methods considered for methane emission reduction are Sequential Transfer of Tank Atmospheres (STTA), using hydrocarbon gas (HC) as cover gas during discharge and control/reduction of the vapour pressure of the loaded cargo. The in-house computer program VOCSim has been used to simulate the improvement potential of operational methods.

3.1.1 Sequential Transfer of Tank Atmospheres

By moving the tank atmospheres from one tank to another, it is possible to increase the content of HC gas in the atmosphere above the crude oil surface, and thus reduce the “driving force” for release of HC gas from the cargo.

The method requires that the cargo tanks of a vessel can be gathered in groups that can be operated in sequence, the more groups the better. To describe the Sequential Transfer of Tank Atmospheres (STTA) in more details, assume that there are three groups of tanks on the vessel.

The unloading is performed as follows:

- Start discharging group 3 while adding exhaust gas to the top of group 3.
- Then discharge group 2. Exhaust gas is still added to group 3 while gas is displaced from the bottom of group 3 to the top of group 2. The cover gas for group 2 contains the HC gas released from the cargo in group 3 during the latter’s discharge.
- Finally group 1 is discharged. Exhaust gas is still added to the top of group 3. Gas is displaced from the bottom of group 3 to the top of group 2, and from the bottom of group 2 to the top of group 1. The cover gas to group 1 therefore contains (most of) the HC gas released both in group 3 and group 2.

When the discharge is finished, there will be almost no HC gas in group 3, only a little HC gas in group 2, and considerably more than “normal” in group 1.

The loading is performed in the “opposite direction”, see Figure 3.1:

- Start loading group 1. Gas is displaced from the top of group 1 to the bottom of group 2, from the top of group 2 to the bottom of group 3, and from the top of group 3 to the atmosphere.
- Then load group 2. Gas is displaced from the top of group 2 to the bottom of group 3, and from the top of group 3 to the atmosphere/ recovery plant.

- Finally load group 3. Gas is displaced from the top of group 3 to the atmosphere/ recovery plant.

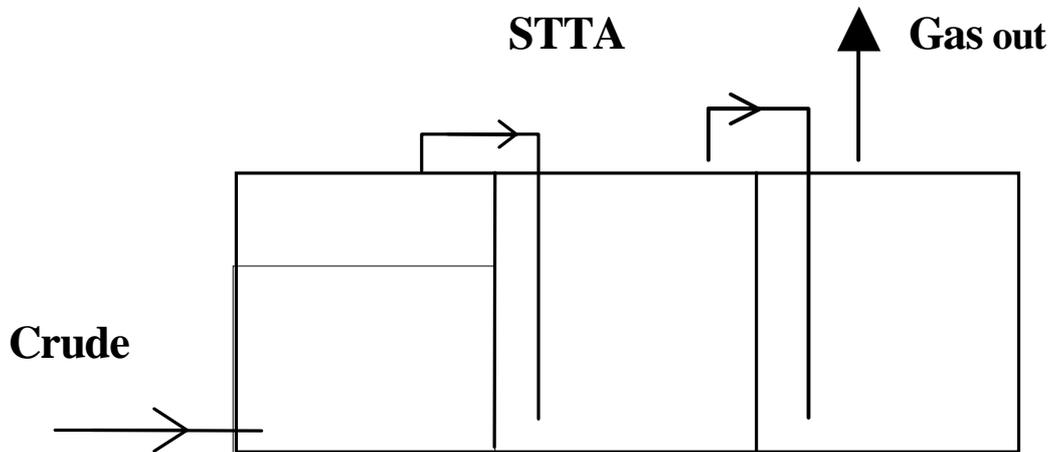


Figure 3.1 Sketch of STTA during loading

While STTA reduces the emission of VOC, it also improves the conditions for a recovery plant, see e.g. Ref 2.

An additional piping system must be installed for the transfer of tank atmospheres. Valves must also be opened and closed during the discharge and loading. Flexibility in tank grouping and the number of remote operated valves needed, will increase the installation costs. Costs from NOK 1 million to NOK 15 million have been mentioned in the past.

Navion ASA holds the patent for the STTA.

To our knowledge, there are only two vessels where STTA are applied. Both are FSOs. As far as we know, the effect of STTA has not been verified by measurements. An offer for verification measurements on the FSO “Nordic Appollo” was recently turned down due to costs.

Simulations have shown that the reduction of VOC emission is significantly dependent on the degree of mixing between the tank atmosphere being in a tank and the gas added to this tank. The less this mixing is, the larger the reduction becomes.

For a situation where application of STTA according to simulations reduces the VOC emission with 13 %, the reduction of the methane emission is only 1 %. In another simulated case with less mixing, the reduction of VOC emission is 44 % and the methane reduction becomes 12 %.

The conclusion is therefore that STTA gives only small to moderate reduction of methane emission.

3.1.2 HC Cover Gas

During discharge a HC gas mixture is added to the cargo tanks. At start of loading, the tank atmosphere will therefore consist of HC gas. During loading the mass of HC gas released from the cargo will be greatly reduced, or may even become negative. This depends on the composition of the cover gas, the tank atmosphere pressure and the bubble point pressure of the loaded cargo.

The VOC emission during loading is approximately equal to the sum of the mass of VOC in the cargo tanks at start of loading and the mass of VOC released from the cargo during loading. Even if the latter part is significantly reduced when HC cover gas is applied, the mass of VOC emitted from the cargo tanks during loading will become larger with HC cover gas than with exhaust gas. Laboratory experiments, full-scale measurements and simulations confirm this. **Therefore the use of HC cover gas is only feasible in combination with other measures, e.g. a recovery plant, energy production or gas return.**

The use of HC cover gas will significantly reduce the volumetric flow rate of gas out of the tanks and provide a more favourable situation for a recovery plant. There is therefore a potential for reduced investment costs, reduced power needed and increased efficiency for a recovery plant.

There are two main challenges in order to apply HC cover gas. They are:

- Where to get the relatively large mass of HC gas needed for the cover gas?
- Safety aspects, classification rules and regulations.

There is one particular area of application where these challenges are more easily met than in general. That is on a FPSO. Due to the presence of the process plant, there will usually be more than enough HC gas available for cover gas, and the HC gas displaced during filling of a tank goes back to the process. Because the FPSO is stationary, permission to use HC cover gas has to be obtained only from the authorities in one country.

There is at least one FPSO using HC cover gas today, Aasgard A. More FPSOs are under consideration for use of HC cover gas, e.g. Norne, Balder and Jotun.

There are two ways of getting hold of the HC gas needed for cover gas that will be mentioned:

- HC cover gas combined with a recovery plant producing liquefied HC gas and storing it onboard until the following discharge. Then the liquefied gas is evaporated to produce cover gas. This is well known technology. An uncertainty is if there will be enough gas available to fill into all the cargo tanks.

- HC cover gas combined with an absorption recovery plant. The HC gas needed for cover gas is “boiled” off from the discharged crude. More work is needed to evaluate all aspects around this “boiling”

Navion ASA has just started a study on HC cover gas applied to shuttle tankers.

Using the simulation program VOCSim, some simulations of the effect on the methane emission of applying HC cover gas have been conducted. As base case has been used a situation with exhaust gas as cover gas. It has a VOC emission of 0.203 wt% (% of loaded cargo) and a methane emission of 0.00357 wt%.

Applying a HC cover gas with approximately the same composition as the HC gas released from the cargo during loading when the cover gas is an exhaust gas, the simulation shows that the VOC emission is increased to 0.325 wt%, or with 60 %. The emission of methane is increased to 0.00855 wt%, or with 140 %.

Removing the methane from the cover gas, but otherwise using almost the same composition as in the previous case, the VOC emission is also now increased to 0.325 wt% or with 60 %. The emission of methane is slightly decreased to 0.00353 wt%, or with 1 %.

To conclude, the emission of VOC from the cargo tanks may significantly increase when applying HC cover gas, while the emission of methane from the cargo tanks will not be reduced, but will more likely be significantly increased. The operational characteristics of the *additional measure that HC cover gas must be combined with*, determines whether the emission of methane to the air will become reduced or not. Refer to section 3.2.5 and 3.3.3.

3.1.3 Vapour Pressure Control

It is obvious that the less the content of light hydro carbons is in the loaded cargo, the smaller will the VOC emission become. With no methane in the loaded cargo, there will be no methane emission. But the reduction of the content of light ends comes at a cost.

The vapour pressure of the loaded cargo is a function of the composition and the temperature of the cargo. Experience has shown that the vapour pressure of the cargo on several offshore fields is above atmospheric pressure when the crude is loaded.

Some simulations have been carried out to show the effect on the emission from reducing the vapour pressure. As base case has been used the same case as in section 3.1.2, i.e. a case with exhaust gas as cover gas, a VOC emission of 0.203 wt% and a methane emission of 0.00357 wt%. The temperature of the loaded cargo is 306 K (=32.85 °C) during loading and 302 K (=28.85 °C) during discharge. The bubble point pressure of the loaded crude at actual temperature (306 K) is approximately 1.59 bara.

Keeping the temperatures unchanged, the vapour pressure can be reduced by reducing the content of light ends. This can be done by changing pressure and/or temperature in (some of) the separators of the process plant upstream of the export point of crude to the tanker. It is beyond the scope of this project to go more into details about this. To obtain some simulation results, the vapour pressure has simply been reduced by means of an “extra” flash.

The original crude was flashed at 1.0 bara and 303.15 K (=30.0 °C). The resulting composition of the produced liquid was then used as composition for the loaded cargo. The emission of VOC is reduced to 0.162 wt%, or with 20.5 %. The emission of methane is reduced to 0.00085 wt%, or with 76 %. The reduction of particularly methane is large. But it comes at a cost. The “extra” flash to bring the bubble point pressure down to 1.0 bara at 303.15 K, removes as much as 0.207 wt% of the cargo as gas. This is 5 times more gas than the mass of reduced VOC emission.

As another example, the original crude was flashed at 1.0 bara and 310.95 K (=37.8 °C). The resulting composition of the produced liquid was used as composition for the loaded cargo. The emission of VOC is now reduced to 0.137 wt%, or with 33 %. The emission of methane is reduced to 0.00043 wt%, or with 88 %. The “extra” flash to bring the bubble point pressure down to 1.0 bara at 310.95 K, now removes as much as 0.465 wt% of the cargo as gas. This is 7 times more gas than the mass of reduced VOC emission. Laboratory experiments, Ref 3, confirm this value.

Of economic reasons the operator of an offshore field usually wants to export the crude oil containing as much gas as possible. Removing light ends to reduce the vapour pressure of the crude may therefore not be the most desired option. An alternative might be to reduce the temperature of the loaded crude.

To see the effect of reduced temperature, a simulation has been performed where the cargo temperature was reduced with 10 K, i.e. from 306 K to 296 K during loading, and from 302 K to 292 K during discharge. The VOC emission goes down to 0.138 wt%, which is a 32 % reduction compared to the base case. The methane emission is reduced to 0.00345 wt%, which is only a reduction of 3 %.

The 10 K cargo temperature reduction reduces the bubble point pressure of the loaded cargo to 1.28 bara. The VOC emission reduction becomes significant, and with a magnitude that is confirmed by model tests, Ref 3. However, the effect on the methane emission becomes very moderate. Considering the possible wax formation problem this cooling may cause, and the costs involved with this cooling, temperature reduction of the cargo does not seem to be an option for methane emission reduction.

3.2 Separation processes

Recovery processes dealt with in this section have the following common features:

- Separation of VOC from the exhaust gas
- “Storage” of the separated VOC gas

3.2.1 Absorption

3.2.1.1 General

VOC gases can be recovered by absorption in pressurized crude oil. Kværner Process Systems (KPS) has a system based on direct absorption in crude oil. Cool Sorption offers systems with absorption in Kerosene and crude oil. For a system with absorption in crude oil only, the VOC/exhaust gas is compressed to about 7-10 bars and fed to a column in counter current flow with crude oil. Theoretically a NMVOC recovery rate of 80-90 % could be obtained. Some of the methane will also be absorbed. Cool Sorption also offers a system with combined adsorption and absorption. This one will be considered in section 3.2.2 covering adsorption technology.

A principle sketch of a system with absorption in crude oil is shown in Figure 3.2.

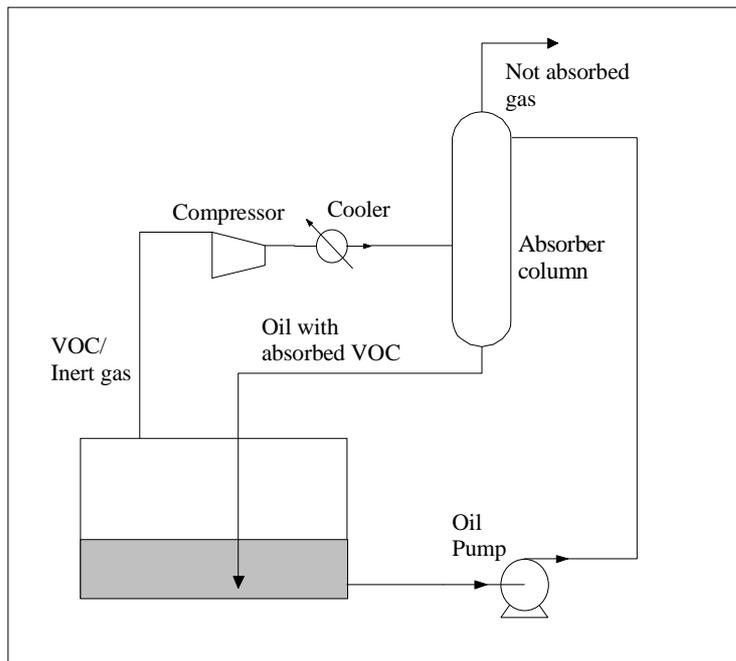


Figure 3.2 Simple sketch of recovery by oil absorption

The recovery can be improved by using a VOC selective membrane on the not absorbed gas to separate the VOC from the exhaust gas. The VOC will pass through the membrane and get re-circulated to the compressor inlet. This will add complexity and cost for the recovery system giving a modest increase of NMVOC recovery and methane. The VOC, including methane, from the membrane could possibly be recovered by cryogenic cooling, refer section 3.2.5.

3.2.1.2 KPS system

The VOC/exhaust gas is compressed to about 10 bars and fed to the column and absorbed in crude oil. Testing of a 1/10 scale recovery plant was done in the period of 1995-96 onboard M/T “Tove Knutsen”. VOC compositions were measured before recovery as well as compositions of the not absorbed gas from the absorption column.

The measurements showed an overall methane recovery of 16-28 % for loading of Statfjord oil. A full-scale prototype has also been installed on M/T “Anna Knutsen”. To improve the recovery of methane, the gas not absorbed could be further treated, for instance by cryogenic cooling and/or by combustion.

3.2.1.3 COOL SORPTION systems

Cool Sorption/Aker has three technologies based on absorption. Two of these combine the absorption in Kerosene and crude oil, the so-called Cold Liquid Absorption (CLA) unit and the Cold Liquid Pressure Absorption (CLPA) unit. The third one is direct absorption in crude oil, similar to the KPS system.

At Sture crude oil exporting terminal a CLA system is installed.

In the CLA system the VOC/Exhaust gas is fed into an absorber with circulating Kerosene at about -25°C . Exhaust gas and methane will follow the off-gas from the column, while the NMVOC will be absorbed in the Kerosene. The Kerosene is fed to a stripper column where the NMVOC is separated and led into an absorber column with crude oil.

A flow diagram for the CLA system is shown in Figure 3.3.

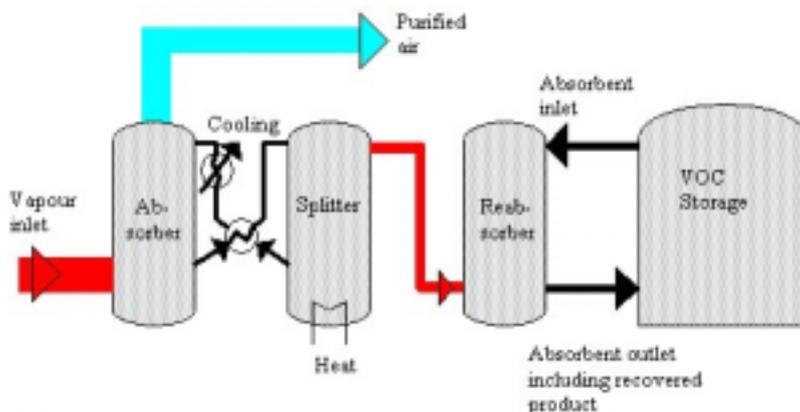


Figure 3.3 COOL SORPTION CLA unit

In the CLPA system the VOC/Exhaust gas is compressed and fed to a crude-oil absorber. The vapour not absorbed is then fed to a Kerosene absorber column. The VOC absorbed in the Kerosene is released in a stripper column and returned to the compressor inlet.

A flow diagram for the CLPA unit is shown in Figure 3.4.

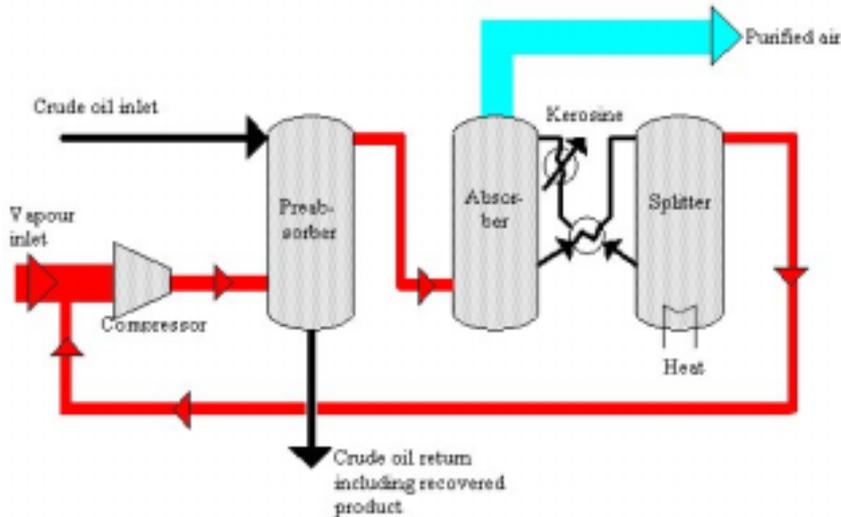


Figure 3.4 COOL SORPTION CLPA system

For further information: <http://www.coolsorption.dk/>

Data for the methane recovery has not been investigated, but are assumed to be small. To recover/handle methane, additional measures must be included. A combination with cryogenic cooling and/or combustion could be further evaluated.

No commercial systems for the recovery of methane from VOC based on absorption alone have been identified.

3.2.2 Adsorption

3.2.2.1 General

The main function of an adsorption system is to separate the hydrocarbon fractions from the exhaust gases. Several technologies are available, but for recovering methane from VOC/exhaust gas mixture, commercial technology is not available. An adsorption system has to be combined with other measures, such as absorption or cooling for handling of the gas.

The SINTEF report “VOC Recovery Based on Adsorption in Crude Oil, A literature study on adsorption and membrane technology” from the VOCON project, Ref 1, contains a literature study on adsorption technology. The conclusion was that relevant literature concerning crude oil operations was scarce. For a more thorough description of adsorption technology it can be referred to this report.

3.2.2.2 COOL SORPTION system

Cool Sorption/Aker offers the Carbon Vacuum Adsorption (CVA) system with adsorption in active carbon. This system is especially interesting for situations with low fractions of hydrocarbons. For high hydrocarbon fractions in feed gas, such a system is not ideal because of size and weight of the equipment. The methane recovery may be in the range of 0 to 5 %. The rest will follow the exhaust gas.

A diagram of the CVA system is given in Figure 3.5.

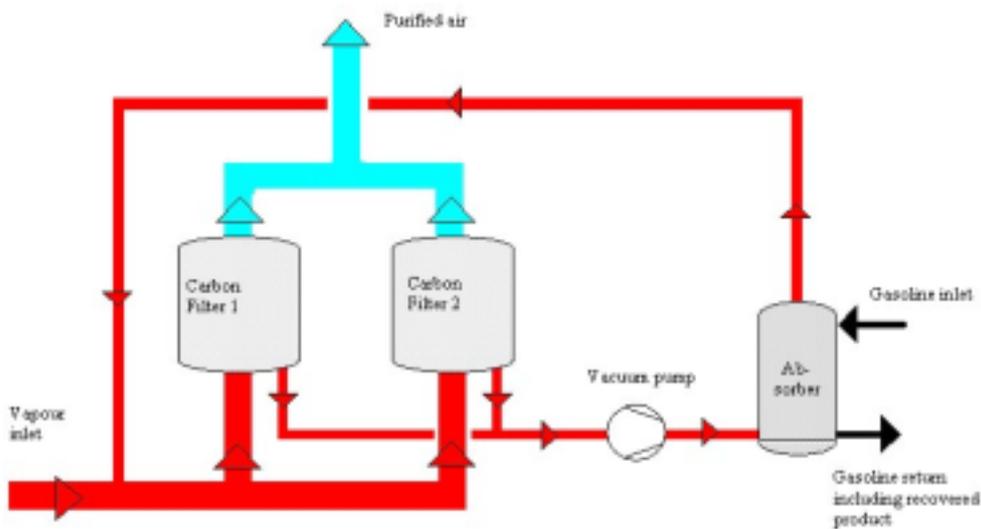


Figure 3.5 COOL SORPTION CVA system

For more information : <http://www.coolsorption.dk/>

3.2.3 Membrane separation

Hydrocarbons and exhaust gas can be separated by use of VOC selective membranes. For recovery of VOC, membrane technology must be combined with other measures, as condensation. Different types of membrane materials, as polymer membranes and rubber membranes are available. The hydrocarbon selectivity increases with increasing carbon number (methane-low selectivity, heavies-high selectivity)

Several commercial membrane processes are available:

VapourSep process	-	Membrane Technology & Researching Inc.
VACONCORE	-	Aluminium Rheinfelden GmbH
Preussag system	-	Preussag Anlagenbau GmbH
Borsig system	-	Borsig GmbH

All of this operates in combination with compression and cooling/condensation. For the recovery of methane none of this systems is expected to be suitable.

ABB Gas Technology AS in Bergen offers VOC recovery systems based on the Borsig technology, mainly for gasoline handling and storage.

GKSS Research Center in Germany has developed a membrane-based system for the recovery of off-gases from gasoline storage.

For a more thorough discussion on membrane technology see Ref 1.

3.2.4 Hydratization

3.2.4.1 General

It has been suggested to recover VOC gases by hydratization in combination with recovery by condensation. Several institutes and companies are working with systems for natural gas hydrates for gas transportation purposes. This can be relevant for VOC recovery where hydrocarbon cover gas is used.

No commercial systems are available for hydratization of VOC. A concept of combining absorption systems with hydratization could be a possibility, but no reference to work on this has been found.

Hydratization as a method of recovering VOC or methane seems not to be a viable alternative because of the complexity of the system and the handling of hydrate in combination with shuttle tanker operation.

3.2.4.2 Statoil concept

Statoil Research Center has had a project with the aim to develop a system for recovering the non-condensed hydrocarbons, including methane, from a re-liquefaction plant. Statoil, Petreco AS and SINTEF Energy Research performed the project in the period of 1996-98. Petreco worked out experimental investigations while SINTEF Energy Research made theoretical studies and process and energy considerations and made also a cost estimate for a prototype plant. A principal sketch of the suggested concept is shown in Figure 3.6.

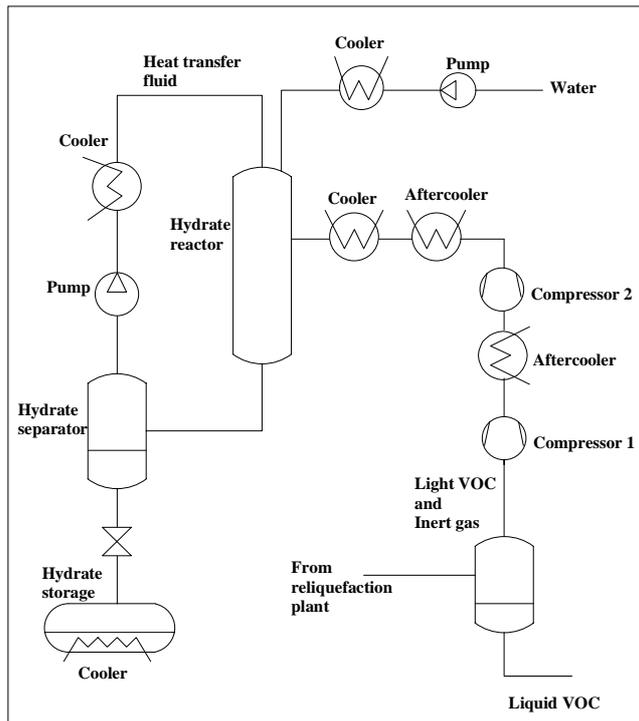


Figure 3.6 Suggested concept for recovery of VOC by hydratization

The project was stopped in 1998 based on the identification of significant technological challenges, energy considerations and cost evaluations.

3.2.5 Condensation

3.2.5.1 General

VOC gases can be recovered by cooling and condensation. The recovery rate of hydrocarbons depends on the operational conditions as temperature and pressure. The use of either exhaust- or HC- gas as cover gas will also influence the recovery rate. In the case of VOC containing water and CO₂, the gas must be dehydrated for cooling below hydrate/freezing point and CO₂ should be removed for cooling below about -80 °C. Potential freezing of heavy hydrocarbons must also be taken into consideration.

A system in principle for recovery by condensation is shown in Figure 3.7.

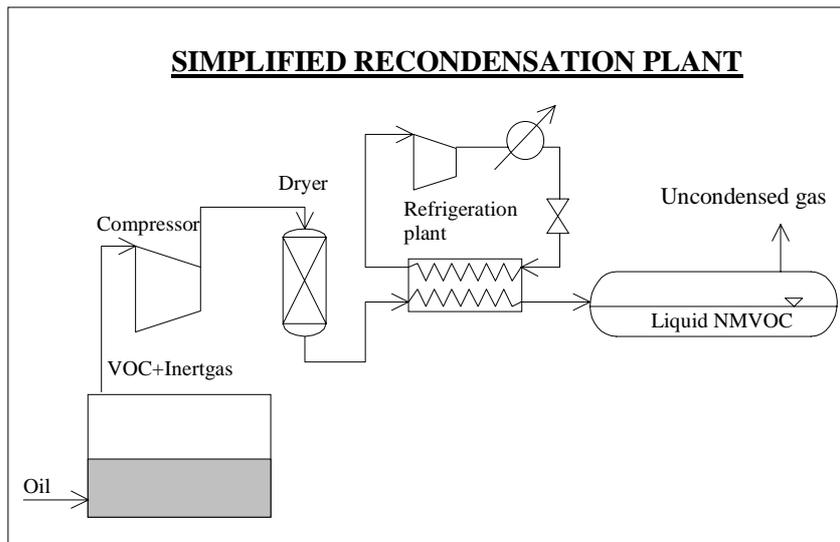


Figure 3.7 Simplified system for recovery of VOC by condensation

The power consumption of a condensation plant is a function of several factors including flow rate and composition of the feed gas and the degree of recovery. Typically the power consumption becomes 2 to 3 MW for a plant on a shuttle tanker when the NMVOC recovery is around 80 % and the loading rate is 8000 m³/h.

3.2.5.2 Recovery potentials

To identify the potential of recovery by condensation and cryogenic cooling, initial calculations have been performed. All are based on VOC compositions typical for the Statfjord field.

Case1, Cooling of total gas flow (exhaust cover gas)

Cooling of total flow at a pressure of 7 bar and 80 % ($\alpha=0.2$) and 20 % ($\alpha=0.8$) exhaust gas content at varied temperatures. The results from the calculation are given in Table 3.1.

For calculating total recovery rates for a loading operation an integration of the total recovery period is needed. Indicative numbers is that cooling to -120°C gives a total methane recovery of around 50 % and cooling to -160°C gives about 85 %.

Table 3.1 Recovery rates by cooling of total VOC+exhaust gas flow, Statfjord VOC, 7 bar pressure

Temperature		Local recovery rate (%)	
		$\alpha=0.2$	$\alpha=0.8$
-40 °C	NMVOG	60.8	93.0
	VOC	59.2	90.9
	Methane	0.9	13.4
-80 °C	NMVOG	90.4	99.0
	VOC	88.0	97.1
	Methane	3.1	31.2
-120 °C	NMVOG	99.2	99.9
	VOC	96.9	99
	Methane	13.1	64.7
-160 °C	NMVOG	100	100
	VOC	98.9	99.9
	Methane	61.2	95.7

Case 2, Two-stage cooling (exhaust cover gas)

Another option is to cool the total flow to a given temperature and further cool only the vapour not condensed in the first part. A calculation based on cooling to -40 °C in a first stage and further cooling of the vapour to -80, -120 and -160 °C has also been performed. The results from the calculations are shown in Table 3.2.

Table 3.2 Recovery rates by two-stage cooling, first stage -40 °C, Statfjord VOC, 7 bar

Temperature in 2 nd stage cooling		Local recovery rate (%)	
		$\alpha=0.2$	$\alpha=0.8$
-80 °C	NMVOG	86.7	97.4
	VOC	84.5	95.2
	Methane	1.8	15,5
-120 °C	NMVOG	98.7	99.8
	VOC	96.2	97.9
	Methane	8.8	28.0
-160 °C	NMVOG	100	100
	VOC	98.6	99.6
	Methane	48.0	83.5

The recovery is somewhat lower compared to cooling the total flow to the same temperature.

Increasing the pressure of the non-condensed gas before cooling will increase the recovery potential. At a pressure of 20 bar, 100 % of the methane (and the other hydrocarbons) will be recovered by cooling to -160°C . Freeze out of CO_2 will be a major challenge with this method, but is not further considered in this report.

There is a potential of recovering significant amounts of methane by cryogenic cooling. This will normally require dehydration and sweetening of the VOC. The recovery potential can be increased if the feed gas to the recovery plant does not contain exhaust gas.

Case 3, Cooling of VOC (Hydrocarbon cover gas)

When hydrocarbons are used as cover gas instead of exhaust gas, any content of N_2 and CO_2 will be small. A more effective recovery can then be obtained. Initial calculations of VOC compositions and flow rate have been used to calculate the recovery potential. The calculations show that very high recovery rates both for NMVOC and methane, only using compression and sea-water cooling, can be obtained.

For a combination of condensation and power production from the non-condensed gas, a cooling to 20°C at a pressure level of 15-25 bar gives a recovery rate that approaches 100 %, both for NMVOC and methane (VOC-composition typical for the Statfjord field). The power produced from the non-condensed gas becomes around 2 MW, which is approximately equal to the power required by the plant.

3.2.5.3 Hamworthy KSE, Concept 1

An almost full-scale recovery plant has been installed onboard M/T “Navion Viking”, operated by Navion. This plant cools the mixture of VOC and exhaust gas to about -40°C . A plant operating at this temperature and at a pressure of 5-10 bars will recover about 1-15 % of the methane contained in the VOC, depending on the local VOC composition and exhaust gas content. The main principle of this concept is as shown in Figure 3.7.

3.2.5.4 Hamworthy KSE, Concept 2

Hamworthy KSE in co-operation with Moss Maritime offers technology for reliquefaction of boil-off gas from LNG and has also offered a plant for liquefaction of natural gas based on this technology. This technology, which is based on the Brayton refrigeration cycle with nitrogen as refrigerant, may have a potential for recovery of methane from VOC. Dehydration and gas sweetening are required.

A Brayton cycle in principle is given in Figure 3.8.

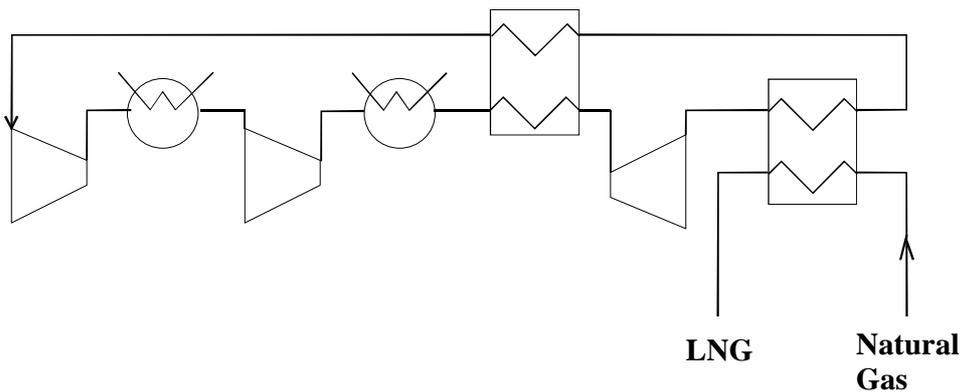


Figure 3.8 *Brayton cycle in principle for the condensation of hydrocarbons*

3.2.5.5 GRS concept

Gas Recovery Systems has in co-operation with SINTEF Energy Research developed a system for recovery of VOC gases by cryogenic cooling, using liquid nitrogen as coolant. This system has been used to recover various gases in mixture with nitrogen with very good recovery rates. The system is very flexible by means of condensation temperature. GRS has constructed one plant with a liquefaction capacity of about 2000 kg/h of pure hydrocarbons. The recovery capacity with 70 % nitrogen in the feed gas is about 1000 kg/h. For a case with 70 vol. % nitrogen and 30 vol. % methane, the consumption of liquid nitrogen is around 6 kg per kg methane. By the use of this plant GRS has with assistance from SINTEF Energy Research performed several commercial recovery operations.

The cold from the evaporating nitrogen is transferred to the VOC gas via a closed circuit with circulating liquid propane. This system can recover gases with a freezing point higher than the nitrogen temperature without freezing occurring. However, water and CO₂ have to be removed to prevent freezing and blocking of heat exchangers. The GRS unit could be combined with other measures (absorption and a first stage cooling) in order to recover methane.

A principle sketch of the GRS system is shown in Figure 3.9

The diagram shows the recovery of VOC during purging of a gas storage tank. Nitrogen vapour is fed at the top of the tank. The gas in the tank is pushed out from the bottom of the tank. In the first period of operation the cargo vapour is pure. After a time nitrogen will be mixed into the cargo vapour. The vapour from the cargo tank is then cooled in the two parallel coolers in heat exchange with cold nitrogen vapour and condensed in the condenser in heat exchange with cold liquid propane, before entering the separator. When the cargo is pure, complete condensation is achieved. When the gas is a mixture with nitrogen some gas is vented from the separator. The condensed liquid is then pumped into the storage (in this case a truck). The system can recover a large variety of gases. The coolant is liquid nitrogen. To avoid freezing of cargo vapours in the heat exchangers, a brine circuit of circulating liquid propane is used and the temperature in the

cargo condenser is controlled by the propane system. This system is commercially available and recovery operations have been successfully performed both on gas carriers and land storage tanks.

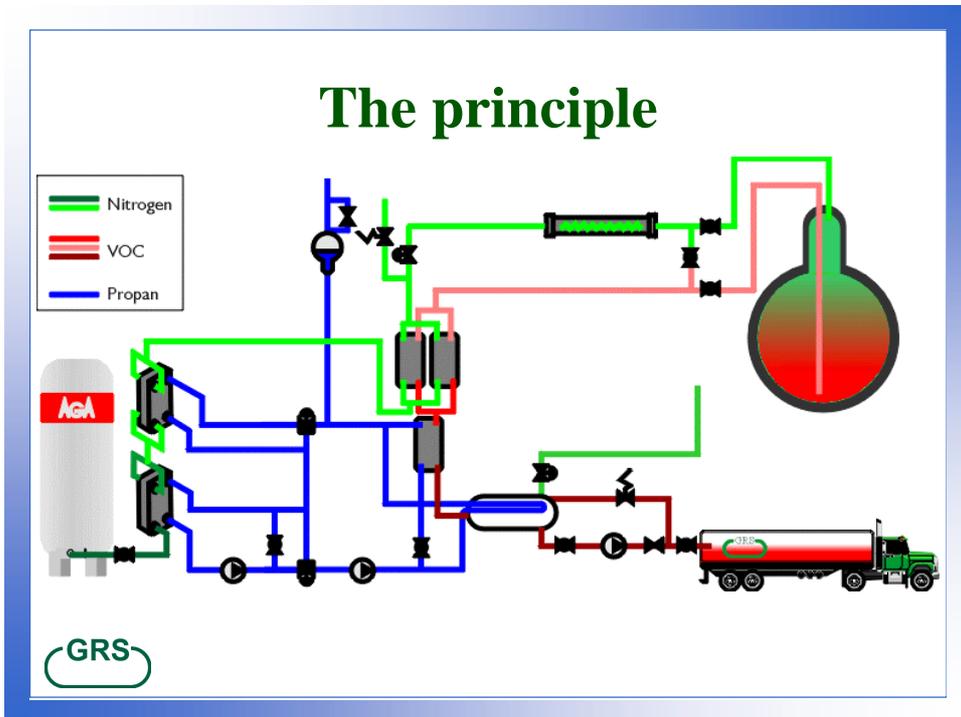


Figure 3.9 Principle sketch of the GRS system

A visualization of the GRS unit is shown in Figure 3.10.

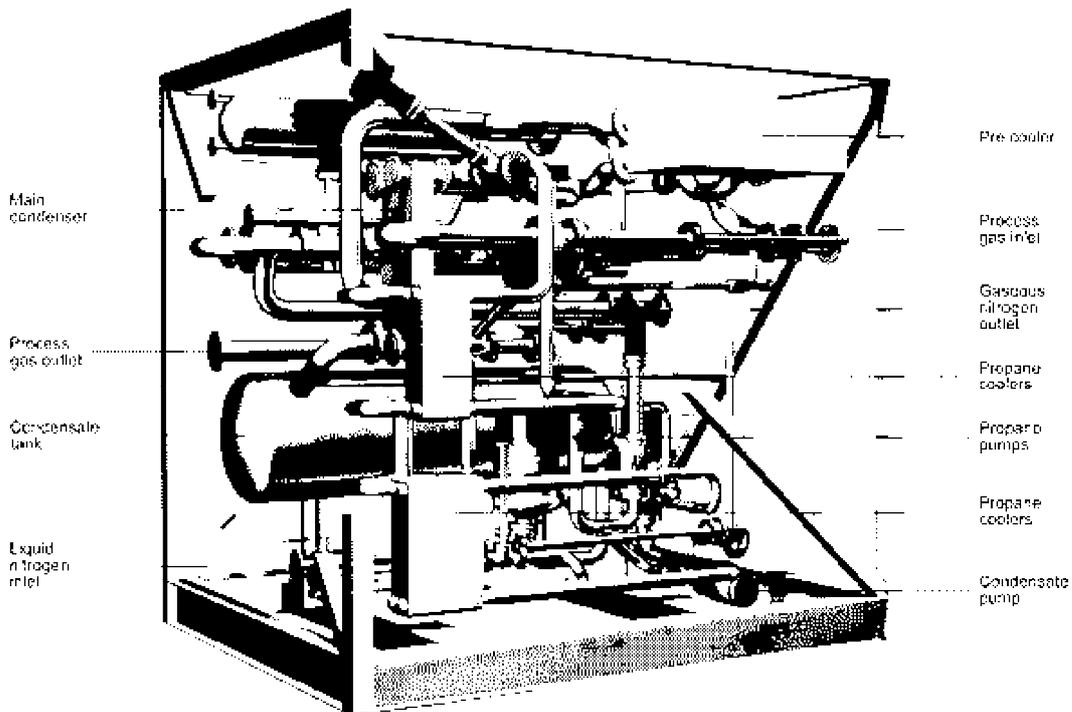


Figure 3.10 *GRS unit for VOC recovery*

For more information of this system: <http://www.skaugen.no>

3.2.5.6 BOC concept

BOC offers the ‘Kryoclean VOC Control System’ for recovery of VOC by cryogenic cooling. This system uses liquid nitrogen as coolant and is an alternative solution to the GRS system in the section above.

A flow diagram of the Kryoclean system is shown Figure 3.11.

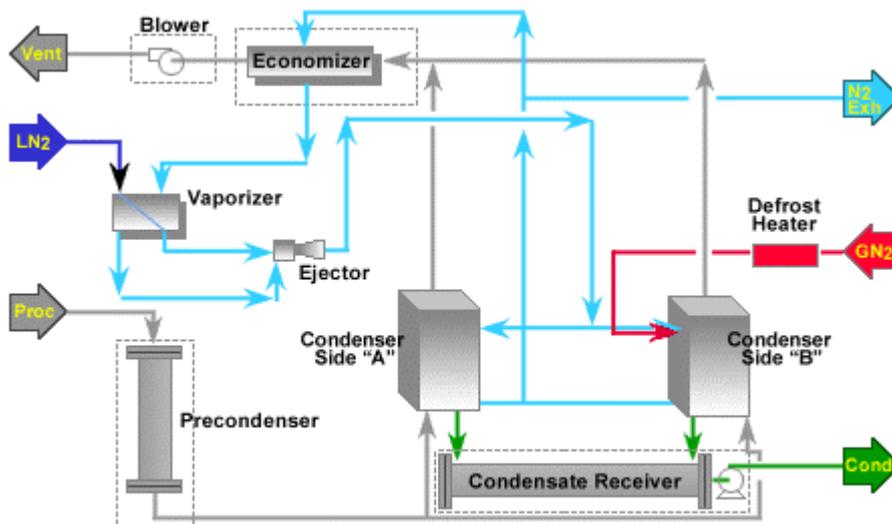


Figure 3.11 *Kryoclean VOC Control System from BOC*

In the Kryoclean VOC control system, dual process condensers are indirectly cooled by vaporized liquid nitrogen for continuous operation to condense VOCs so they can be removed as liquids. The dual condenser system permits some degree of freezing in the condenser. One condenser is in operation while the other is defrosted.

More information can be found at <http://www.boc.com/kryoclean/control/control.htm>.

3.2.5.7 AGA/LINDE system

AGA/LINDE offers the CIRRUS® VEC (Vapour Emission Control) for cryogenic recovery of VOC with use of liquid nitrogen as coolant like the GRS and BOC system.

For more information:

<http://www.aga.com/se>

<http://62.27.58.14/en/p0005/p0044/p0044.jsp#cyro>

3.3 Combustion methods

The part of the gas emitted during loading from the cargo tanks being VOC can be flared or burned to produce energy. For most shuttle tanker operation, the latter option will produce much more power than can be utilized onboard the tanker during loading. A more realistic approach is to combine power production with a recovery plant, using only the part of the gas not recovered for power production covering the power consumption of the recovery plant. Such combinations are focused in this report.

When exhaust gas is used as cover gas, the power consumption for a recovery plant on a shuttle tanker typically in the range of 2 to 3 MW when the NMVOC recovery is around 80 % and the loading rate is 8000 m³/h. Using hydrocarbons as cover gas, the power required for the same degree of recovery will be reduced significantly (actual level has to be calculated).

3.3.1 Gas quality

The gas quality available for combustion will vary dependent on e.g. on the type of crude oil loaded, the crude oil on the previous voyage and the recovery process during the loading. With exhaust gas as cover gas, the emitted gas has a large amount of N₂ and CO₂ that give a low calorific gas for burning.

If HC gas was used as cover gas in the crude oil tanks, the gas available for combustion would consist more or less of pure HC components, which would be beneficial for a set of different combustion processes.

Table 3.3 gives examples of composition and properties of the gas coming out after different VOC recovery plants. The compositions are from measurements and simulations on the Statfjord field.

Table 3.3 Typical values of un-recovered gas

		Absorption Plant		Condensation Plant	
		Exhaust cover gas	HC cover gas	Exhaust cover gas	HC cover gas
Components (mol %)	N ₂	62	0	73	0
	CO ₂	2	0	10	0
	O ₂	3	0	4	0
	C1	20	60	2	15
	C2	5	15	3	50
	C3	5	15	5	28
	C4+	3	10	3	7
LHV (kJ/kg)		15000	48000	8000	47000
Methane number			41		39

The composition of the VOC part of the un-recovered gas will also vary significantly over the time that the recovery plant is running (during loading), see an example in Figure 3.12. It is especially the amount of methane that varies considerably.

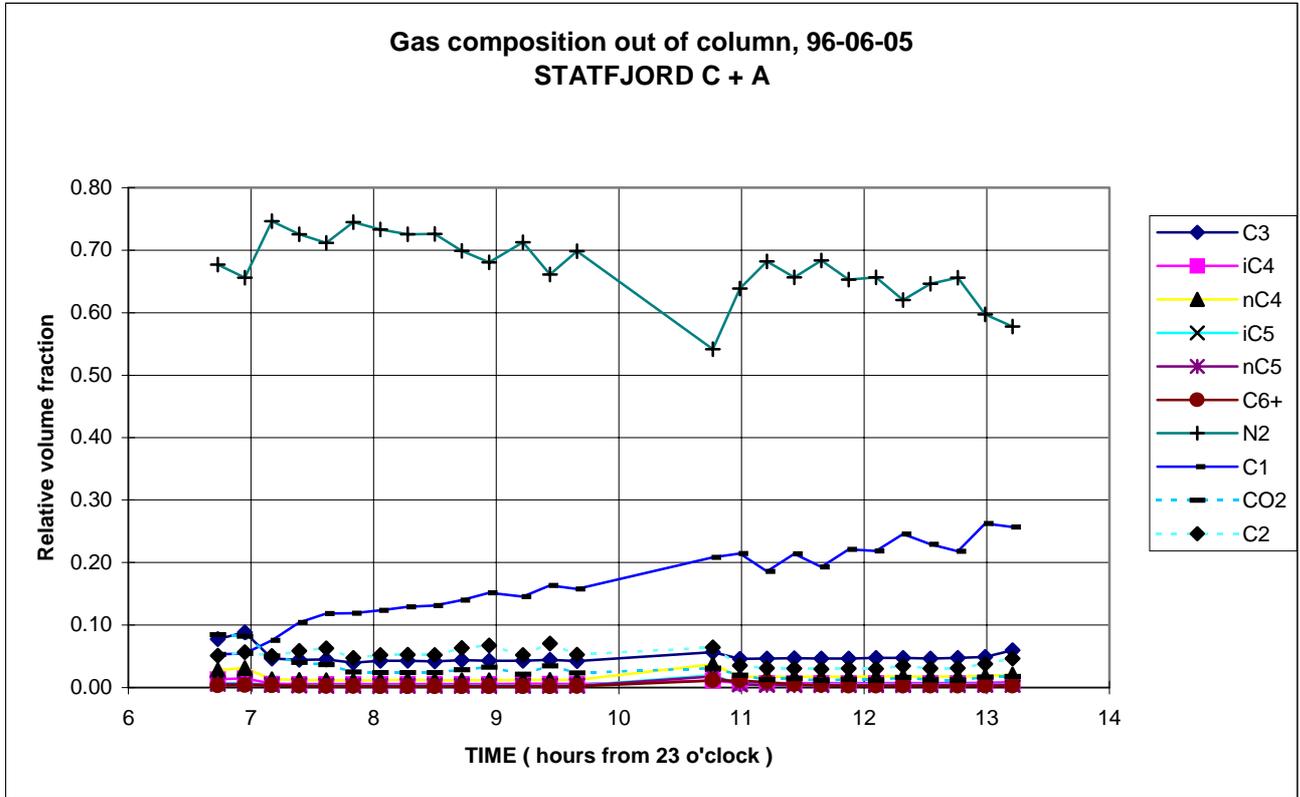


Figure 3.12 Example of composition of un-recovered gas downstream of an absorption recovery plant.

3.3.2 Flaring

Flaring systems can be adapted to burn un-recovered gas from a recovery plant. Flaring is relatively easy to implement, and is not much sensitive to gas quality or variations in the amount available. Flaring systems for burning these gas qualities is considered as state of the art technology.

Flaring will reduce the environmental impact of the emission because the emission of methane is considered to have around 23 times greater effect as a green house gas compared to the CO₂ produced when the methane is burned. However, flaring is not considered to be an optimal solution since it gives no use of the energy produced, and is therefore not beneficial regarding environmental impact.

3.3.3 Power production:

The power that can be produced from the un-recovered gas is probably best utilised in a power pack with direct pulling of the VOC recovery plant onboard the vessel.

Power produced could be connected to the el-system onboard the ship and supply power like any auxiliary generator set. This would give a more flexible solution to be optimised for power demand, availability of un-recovered gas. Integration with the el-power system onboard an existing vessel is, however, considered to be complex and costly. When designing a new shuttle tanker, this option should be considered.

The un-recovered gas represents a significant amount of energy that could be transformed to electric power. When exhaust cover gas is used, the un-recovered gas is a low calorific gas, and the available amount of gas is large compared to the case where hydrocarbons is used as cover gas. The gas in the latter case has higher specific energy. Burning the un-recovered gas and producing useful energy is an intriguing way to treat an unwanted emission of methane.

Please keep in mind that the un-recovered gas is in the **gas phase** when different ways of power production are evaluated below.

3.3.3.1 Steam turbine

Exhaust gas as cover gas

As shown in table 3.3 the un-recovered gas could vary a lot depending of the recovery technique and even more depending of the oil field, but they can all be burned in a steam boiler. The burner has to be arranged with pre-combustion system, to obtain the necessary temperature and flame stability in the main combustion, which is then fired with the lean low calorific un-recovered gas. The pre-combustion fuel could be diesel oil or a part of the recovered liquid hydrocarbons.

To cope with the variation in gas quality and amount available, special attention has to be paid to the burner regulation. Feedback from O₂ sensors in the exhaust gas will be needed. This technology is well known, and principally it is relatively straightforward to burn this type of gas in a steam boiler.

Along with the boiler comes a super-heater, a steam turbine with or without a generator, a condenser, water treatment equipment etc. Complete systems in the range of 2 - 4 MW is not common and have to be tailor made. Such a system is flexible in operation and does not require additional pressure build up of gas supply.

A steam turbine either for power production or as direct prime mover of rotating equipment can be foreseen. However, the challenges are to bring down complexity and cost for such a steam turbine plant. Today only large-scale power plants are using this technology.

Hydrocarbons as cover gas

In the case of un-recovered gas from a recovery plant where hydrocarbons is used as cover gas, the gas will be closer to standard gas qualities and hence standard gas burners could be used. With regard to a complete power production system, the considerations are the same as above.

3.3.3.2 Gas turbine

Exhaust gas as cover gas

When exhaust gas is used as cover gas, the un-recovered gas will contain 60-70% N₂ and some CO₂. This lean and low calorific gas could be burned in a gas turbine, but it has to be re-designed, especially the combustor. The temperature in the combustor will be the limiting factor when running on the lean low calorific gas. A combustion temperature below 1800 °K (normally obtained by a fuel/air ratio higher than 0.4), means penalty in efficiency and emissions. A re-design has to consider an increase in gas flow. The change in gas quality also during the loading sequence will be a challenge.

Further, the gas supply has to be considered. A relatively high flow of gas must get a significant pressure build up (from about 10 bar to 20-25 bar).

A gas turbine for these variable low calorific gas qualities is not considered to be feasible.

Hydrocarbons as cover gas

In the case of un-recovered gas from a tanker using hydrocarbons as cover gas, the situation is quite different. Standard gas turbines could be used. There are some suppliers in that power range. However, the need of higher pressure (20-25 bar) requires a gas booster.

3.3.3.3 Gas engines

Exhaust gas as cover gas

Gas engines for low calorific gases are state of the art. Even as low as 8000 kJ/kg has been used as fuel for gas engines. The gas engine concept used is the homogeneous charge (premixed gas/air) with pre-chamber spark plug system or diesel pilot ignition system. In the power range of 2-4 MW it could be different configurations; one, two, three and even more units to cover the load range.

The gas supply system has to be designed in each case. The gas is available at high pressure (about 10 bar), which makes it easier to adapt a sufficient system without any need for gas boosting.

The variation of gas qualities also during the loading sequence, requires a more sophisticated control system with some kind of feed back information (e.g. calorimeter). The engine has to be

sized to meet the lowest calorific value and will therefore have a relatively low power/weight factor.

The gas-diesel concept is more robust with respect to the variations in gas quality, but will add extra complexity and cost, e.g. in the fuel supply a high-pressure compressor (350 bar) will be needed. By proper sizing of engine versus “worst” gas quality, a proper control system, and utilising the low charge air temperature that can be obtained offshore, the premix concept as described above is evaluated to be a better choice. Such engines with diesel back up are also available.

Hydrocarbons as cover gas

The rich un-recovered gas from a system with hydrocarbons as cover gas can be burned in standard gas engines, preferably lean burn gas engines with pre-chamber spark plug system. The challenge is the low methane number (MN approx. 40), which means the engine has to be de-rated compared to high methane number gases (MN 80). Control system with knocking sensors is required.

The power could typically be produced from one, two or three engine units. The gas pressure available (10 bar) is ideal for gas engine supply.

4. RECOMMENDATION

4.1 Recommended Recovery Processes

No single/simple processes have been found that will significantly reduce the emission of methane. It seems that a combination of processes will be needed to obtain this objective.

The use of HC gas instead of exhaust gas as cover gas combined with other processes, seems very promising from a technical point of view. The question of safety and regulations in conjunction with HC cover gas is of course an obstacle. The fact that it is in use on the Aasgard FPSO indicates strongly that it is possible to get permission to use HC cover gas. But it will take some time to carry it through. Therefore a process has also been recommended for the exhaust cover gas case.

4.1.1 Exhaust gas as cover gas

The combination of a recovery plant and power production from the un-recovered VOC, is the recommended process. The recovery plant can either be an absorption plant where recovered VOC is “stored” in the cargo, or it can be a condensation plant where the liquefied VOC is used for propulsion, re-injected in the cargo during unloading or during the loading if the storage tank is full, or sold as a product.

The power produced from the un-recovered VOC is primarily intended to cover the power needed by the recovery plant. The un-recovered gas can be burned to produce steam for a turbine, or used as fuel for a piston engine. Steam turbine technology is available, but no commercial product in this power range exists, and must be made for the purpose. Gas engines for low calorific gases need a minor adjustment to be able to operate on the actual gas, and will be the recommended power system.

The combination of exhaust cover gas, recovery plant and gas engine run on the un-recovered gas, seems to be the only combination commercial available to day for a significant reduction of the methane emission that do not need considerable development work, or rules and regulation changes.

4.1.2 Hydrocarbon as cover gas

Of the combined processes reviewed, the combination of HC cover gas, recovery plant and power production from the non-recovered VOC seems most promising from a technical point of view.

The recovery plant can be an absorption plant where recovered VOC is “stored” in the cargo. The use of HC cover gas will reduce the rate of the feed gas and the pressure in the absorption process. The process will require less power, and the investment costs for the plant will be reduced.

A condensation plant can also be combined with HC cover gas and power production from the un-recovered gas. Contrary to the case with exhaust cover gas, only seawater cooling may be required, simplifying the plant considerably. The liquefied VOC is used for cover gas.

Power can be produced from the un-recovered gas by means of a piston engine, which in this case will be commercially available technology. A gas turbine or a steam turbine is also an alternative.

The power production may seem to increase the complexity of the recovery plant. But it must be remembered that most of the existing shuttle tankers have too little electric power available for a recovery plant. Additional power generation must therefore be installed, and the preference seems to be a separate and dedicated power pack. Utilising the VOC that otherwise will be emitted to the atmosphere as fuel for this power pack, is beneficial for the environment.

4.2 Further Work

If HC cover gas is considered for application, more work is needed on how to obtain the required amount of gas during discharge, and how the flow and composition of gas out of the cargo tanks will become. During this work, one must take into consideration that a shuttle tanker may load on different fields with different crude compositions etc.

The subjects of safety, rules and regulations for application of HC cover gas will need more work

More work is also needed on the power production subject, particularly when an exhaust gas is used as cover gas.

Recovery by cryogenic cooling has the potential to recover a high fraction of methane released from the oil. When exhaust gas is used, solutions for the handling of CO₂ must be found. Also water contained in the gas must be considered. It is suggested to analyze in more detail the use of cryogenic methods, using liquid nitrogen, in combination with other recovery methods:

- Combined with re-liquefaction plant with and without membrane separation and power production
- Combined with absorption in crude oil with and without membrane separation and power production

The purpose is to come up with a conclusion concerning overall potentials for the use of cryogenic cooling, in combinations with other measures, for methane recovery.

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