TERPENES IN BIOGAS PLANTS DIGESTING FOOD WASTES

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Terpenes in Biogas Plants Digesting Food Wastes

Study to Gain Insight into the Role of Terpenes

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Foreword

The aim of this study has been to contribute to a better understanding of the production of biogas and biomethane from food waste. The results give an overview on the fate of terpenes present in the food waste during the biogas production as well as during the production of biomethane from this biogas.

The study delivers an important piece to the puzzle in order to understand how to minimize the health risks and process problems connected to the presence of terpenes in the biogas production.

Karine Arrhenius, SP Swedish Research Institute, has been project leader of this project. The project was conducted by SP in collaboration with My Carlsson, Veolia Water Technologies AB. The project has been supported by a reference group from industry in biogas production and upgrading as well as suppliers of equipment. The group consisted of:

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Sammanfattning

Vid biologisk nedbrytning av organiskt material under syrefria förhållanden (rötning) bildas biogas, vars huvudkomponenter är koldioxid och metan. Biogasen innehåller också många andra gasformiga substanser, men i mycket lägre koncentrationer. En del av dessa substanser har oönskade egenskaper relaterade till lukt, miljö och hälsa och kan orsaka problem både för den mikrobiologiska processen och för den utrustning som används i anläggningen. Förekomsten av dessa föroreningar har visats vara starkt kopplat till det organiska materialets (substratets) sammansättning. Terpener har visats vara de dominerande organiska föroreningar som bildas när biogas framställs av matavfall. I synnerhet har pcymen och D-limonen rapporterats utgöra upp till 90% av alla flyktiga organiska föreningar i biogasen. Dessa ämnen finns också i många andra flöden i biogasanläggningar, såsom kondensat, substratet, rötresten, luften i omgivningen mm. Ett antal problem har förknippats med dessa terpener, inklusive luktproblem, inomhusluftens kvalitet (arbetsmiljö) och driftproblem.

Syftet med studien var att få fördjupad insikt i den roll som terpener har i biogasanläggningar där matavfall rötas genom att undersöka hur terpener kommer in/bildas i biogasanläggningar och var de hamnar beroende på substratets sammansättning och processdesign, med fokus på deras öde under produktionen av biometan. Dessutom undersöktes terpeners effekter på utrustning och arbetsmiljö.

Metod

I den första delen av studien vidareutvecklades analysmetoder för detektion och kvantifiering av terpener i gasprover, processvatten och substrat. Metoderna har ett gemensamt sista steg som utgörs av analys med Termisk Desorption-Gaskromatografi-Masspektrometri/Flamjonisationsdetektor (TD-GC-MS / FID) efter adsorption av terpener på Tenaxrör. Analysmetoderna tillämpades sedan på prover av substrat, biogas, kondensat, biogödsel och biometan som samlades in från 8 olika svenska biogasanläggningar där matavfall rötas. 3 av dessa hade en termofil process (rötning vid 55°C) och 5 hade mesofil process (rötning vid 35°C). Dessutom utfördes satsvisa rötningsförsök med substrat från en av de deltagande anläggningarna för att möjliggöra massbalansberäkningar och undersöka inflytandet av substratsammansättning och rötningstemperatur på sammansättningen och mängden terpener i biogasen under kontrollerade former. Terpeners effekter på utrustning undersöktes genom exponeringstester där gummipackningar av två olika gummimaterial (Nitrile Butadiene Rubber - NBR och Epichlorohydrine Rubber - ECO) utsattes för D-limonen och p-cymen i gasrespektive vätskeform, varefter effekten på gummits hårdhet och volym utvärderades. För utvärdering av arbetsmiljöeffekter utfördes fältmätningar där halten av terpener i utrymmen där personal kan exponeras analyserades.



Resultat

D-limonen visade sig vara den dominerande terpenen i de studerade substraten. Det var i vissa fall svårt att få reproducerbara resultat med den utvecklade metoden och i de fall resultaten mellan replikat varierade alltför mycket användes inte dessa tester vid utvärderingen. I samtliga fall där resultaten bedömdes acceptabla utgjorde dock D-limonen mer än 90% av alla terpener som uppmättes i substratetet, medan p-cymen utgjorde ca 1%.

I rötresten var istället p-cymen den dominerande terpenen och utgjorde mer än 90% av alla terpener som uppmättes. Koncentrationen av de 4 dominerande terpenerna i biogasen som samlades in från de 8 anläggningarna presenteras i Fig. S1. P-cymen var klart dominerande i biogasen som produceras vid mesofil rötning med ett undantag där D-limonen var klart dominerande. Däremot var förhållandet D-limonen/p-cymen mer balanserat vid termofil rötning. Ett positivt samband mellan andelen matavfall i det behandlade substratet och mängden terpener som uppmättes i biogasen påvisades. Koncentrationen terpener ökade linjärt med andelen matavfall upp till 70%, varefter den jämnades ut (Fig. S2). Koncentrationerna av terpener som uppmättes varierade från 360 mg/m³ upp till 1650 mg/m³. Stora årliga variationer observerades och dessa tycktes vara korrelerade med konsumtionen av citrusfrukter. Detta behöver verifieras med ett större urval av prover (förslagsvis månadsvis provtagning under ett år vid minst fem anläggningar).



Figur S1: Koncentration av terpener i biogasprover från 8 biogasanläggningar (5 mesofila och 3 termofila).





Terpener / andelen matavfall i det behandlade substratet

Figur S2: Koncentration av terpener i biogasprover plottade mot andelen matavfall I det behandlade substratet.

Koncentrationen av terpener i biometan varierade från 240 mg/m³ ner till 5 mg/m³. Reduktionsgraden (procentuell andel av terpener som avlägsnats från biogasen) för de olika uppgraderingsteknikerna beräknades till:

- Vattenskrubber: 96%, 83%, 95%
- PSA: ~100%
- Aminskrubber: 71%, 85%, 61%

Det bör nämnas att endast småskaliga aminskrubbers utvärderades i denna studie. I storskaliga aminskrubber kyls gasen ofta till 5°C, vilket leder till att reduktionsgraden då är jämförbar med de övriga teknikerna.

Resultaten från satsvisa försök visade en tydlig skillnad i terpensammansättningen i biogas producerad från identiska substrat, men under olika rötningstemperatur (mesofil respektive termofil). Andelen p-cymen var betydligt högre i biogas som producerats under mesofila temperaturförhållanden (Tabell S1).

Tabell S1: Fördelning	g mellan D-limonen and	p-cymen i biog	as producerad vid	satsvisa rötningstester.
raben ozri i oracining	S menun B mnonen ana		as producerda via	Satsvisa i otimigstesteri

•				•
	Test 1 (Maj)		Test 2 (Sep	tember)
	D-limonen	p-cymen	D-limonen	p-cymen
Mesofilt test	40%	60%	40%	60%
Termofilt test	80%	20%	100%	0%
Mesofilt test med spetsat substrat	65%	35%	60%	40%
Termofilt test med spetsat substrat	85%	15%	100%	0%

Massbalansberäkningar för terpener, D-limonen samt p-cymen utfördes för att utreda hur stor andel av terpenerna i substratet som övergår till gasform och i



vilken utsträckning D-limonen omvandlas till p-cymen under olika förhållanden (Tabell S2). Beräkningarna baserades på Test 1 där substratet innehöll ca 20% matavfall och det spetsade substratet hade 5% extra D-limonen tillsatt i form av finrivet yttersta delen av apelsinskal. Resultaten visar att mängden terpener är 6 till 8 gånger högre i det ursprungliga substratet än i gasen. Endast en liten tillsats av 5% extra D-limonen ger en oproportionerligt stor ökning av terpener i biogasen. Det finrivna apelsinskalet släpper troligtvis lättare ifrån sig terpener, men troligtvis är osäkerheten i mätningen av terpener i substratet en del av förklaringen. Helt tydligt är dock att mängden p-cymen i gasen är betydligt högre än i substratet, vilket visar att denna förening bildas i reaktorn.

μg	Mesofil		Termofil		
	Substrat	Spetsat substrat	Substrat	Spetsat substrat	
Terpener i biogas	75	208	60	195	
Terpener i substrat	491	511	491	511	
Terpener substrat/terpener gas	6,5	2,5	8,2	2,6	
D-limonen i biogas	29	125	43	157	
D-limonen i substrat	470	489	470	489	
D-limonen substrat/D- limonen gas	16,2	3,9	10,9	3,1	
p-cymen i biogas	40	71	11	28	
p-cymen i substrat	4,7	4,7	4,7	4,7	
p-cymen substrat/p-cymen gas	0,1	0,1	0,4	0,2	

Tabell S2: Mängden uppmätta terpener, D-limonen respektive p-cymen i substraten som användes i satsvist test 1 samt i den producerade biogasen. Beräknat förhållande mellan mängd i substrat och mängd i gas.

*mätningen misslyckades

Exponeringstestet visade att exponering för terpener i gasfas inte påverkade gummimaterialens volym, men ett av materialen, NBR, blev avsevärt hårdare efter exponering. Exponering för kondensat innehållande terpener orsakade främst uppmjukning av gummimaterialet, men även en viss volymökning. I detta fall påverkades den andra gummitypen, ECO, mest.

Uppgraderingsanläggningen visade sig enligt frågeformulären vara den mest relevanta platsen för att utvärdera exponeringsrisken för terpener. Fördelningen av terpener uppmätta i arbetsplatsmiljöer speglade fördelningen av terpener som uppmättes i biogas från motsvarande anläggning. Arbetsplatserna hade låga terpenkoncentrationer av högst 20 mg/m³, långt under det hygieniska gränsvärdet. Alla uppmätta halter var mycket högre än rapporterat tröskelvärde för lukt. Drifttekniker rapporterade förekomst av starka obehagliga lukter samt identifierade huvudvärk vid långvarig vistelse i vissa områden som den allvarligaste hälsorisken relaterad till terpener.



Sammanfattande slutsatser

- Halten terpener i biogas är proportionell mot andelen matavfall i det behandlade substratet (upp till 70%) oberoende av rötningstemperatur.
- Koncentrationen av terpener i biogasen varierar över året, troligtvis korrelerat till konsumtionen av citrusfrukter
- D-limonen är den dominerande terpenen i substraten, medan p-cymen dominerar i rötresten, vilket indikerar att p-cymen bildas från D-limonen under rötningen. I mesofila processer hinner oftast den största delen av Dlimonen omvandlas till p-cymen under rötningen, medan en större andel av Dlimonen avdunstar till gasen innan omvandling i termofila processer. Skillnaden i omvandling kan förklaras dels av temperaturskillnaden, dels i skillnaden i mikroflora.
- Den största andelen terpener från biogas återfinns i processvattnet eftersom de flesta uppgraderingsteknikerna effektivt avlägsnar terpener från biometan.
- Gummimaterials egenskaper påverkas när de exponeras för terpener, framförallt i vätskefas.

Halterna av terpener i arbetsmiljöer underskrider hygieniska gränsvärden men kan orsaka problem i form av obehagliga lukter och huvudvärk.



Summary

The project aimed to gain insight into the role of terpenes in biogas plants where food waste is digested by investigating how terpenes enter/ are formed in the biogas plant and where they end up depending on substrate composition and process design, with focus on their fate during the production of biomethane. Furthermore, terpenes' effects on equipment, workplace environment and end users were examined.

Terpenes have been shown to be the main organic impurities formed when biogas is produced from food waste. In particular, p-cymene and D-limonene have been reported to represent up to 90% of all VOCs in the biogas. These substances are also found in many other flows in these biogas plants, such as the condensate, the substrate, the digestate, the air in the surroundings etc. A number of problems have been linked to these terpenes, including odor problems, indoor air quality issues at workplaces and operational problems.

In the first part of this study, analytical methods for the detection and quantification of terpenes in gas samples, process water samples and substrates have been further developed. The methods have a common final step consisting of a Thermal Desorption-Gas Chromatography-Mass Spectrometry/Flame Ionization Detector (TD-GC-MS/FID) analysis using Tenax TA for the trapping of terpenes.

The methods were then applied to samples taken at 8 different biogas plants where food wastes are digested. Samples of substrate, biogas, condensate, digestate and biomethane were collected. Batch trials were also set up in order to perform a mass balance and to investigate the influence of the substrate composition and the digester temperature on the concentration of terpenes in the biogas under controlled conditions.

p-cymene was found to be clearly dominant in the biogas produced during a mesophilic digestion with one obvious exception where D-limonene was clearly dominant. On the contrary, the ratio D-limonene/p-cymene was found to be more balanced when the biogas is produced by a thermophilic process. Large annual variations were observed which seemed to be correlated with the consumption of citrus fruits. D-limonene was clearly the dominant terpene in the substrates whereas p-cymene was found to be the dominant terpene in the digestates. These results suggest that p-cymene is converted from D-limonene during digestion of the substrate. Concentrations of terpenes in biomethane (240 mg/m3 down to 5 mg/m3, significantly higher than most of the reported odour threshold values for terpenes) depended upon the upgrading method; in this study, the results suggest that PSA and water scrubbers were more efficient to remove terpenes than amine scrubbers. It is worth to notice that only smaller scale amine scrubbers were tested in this study. With larger amine scrubber units, the gas is cool down to 5°C and the removal efficiency will most certainly be comparable to the removal efficiency from the other techniques. Studies with a larger base and shorter time intervals between sampling occasions need to be undertaken to deepen the conclusions proposed here.



The distribution of terpenes measured in workplace environments mirrors the distribution of terpenes in the biogas. The workplaces showed low terpene concentrations of max 20 mg/m3, largely below the occupational exposure limit. Monoterpene concentrations in the vicinity of worker performing different tasks were quite low as well. However, the concentration of terpenes was found to be higher than recommended short-term values in a confined space at one plant, despite relatively high exposure limits set for terpenes. Rubber materials studied here were shown to be affected in a terpene environment (mostly when exposed to condensate containing terpenes).



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1 Background

1.1 TERPENES IN BIOGAS PLANTS

During the production of biogas from substrates such as food waste, sewage sludge, manure and other organic waste, the organic material is broken down to the main end products, methane and carbon dioxide. However, biogas also contains many other gaseous substances [1, 2], but in much lower concentrations. Some of these substances have undesirable odors and may be harmful to the process, the environment, the human health and the equipment. Terpenes, in particular p-cymene, and D-limonene, have been shown to be characteristic for biogas produced in facilities where food waste is digested [3]. It has also been shown that some of these terpenes follow in the vehicle gas, biomethane, when the gas is upgraded to fuel quality [3]. The concentrations of terpenes present in biomethane depends on the substrate, the biogas process and the upgrading technique. These substances are also found in the process water, such as the condensation water recovered after the drying stage [4] and in samples of air in some locales at the plant.

A number of problems have been linked to terpenes in biogas plants, including odor problems, indoor air quality issues at workplaces and operational problems. The concentration of terpenes in the biomethane can be high enough to impact/mask the odorisation of the fuel by compounds as tetrahydrothiophene (THT) despite terpenes odor threshold being 1,000 times lower than those of tetrahydrothiophene, THT [5]. At high concentrations, terpenes may also condensate in the natural gas pipelines and influence the integrity of the plastic pipelines and the components in the gas grid [5]. Regarding terpenes' impact on the equipment, some Swedish plants have suspected these substances to partly have dissolved electrical cables and other rubber / plastic parts in valves and pumps, resulting in difficulties to operate valves and consequently need to replace damaged components with shorter time intervals. Furthermore, compensators with rubber which are sitting after blowers have been reported to have been damaged by terpenes. Regarding issues related to workplace environment, monoterpenes are irritating to skin and mucuous membranes and can cause both allergic and nonallergic contact dermatitis. The occupational exposure limit in Sweden is 150 mg/m³ for both total and individual monoterpenes [6, 7].

The project aimed at gaining insight into the role of terpenes in biogas plants where food waste is digested by investigating how terpenes enter / are formed in the biogas plant and where they end up with focus on their fate during the production of biomethane. Eight different plants across Sweden participated in this study. Both mesophilic and thermophilic processes participated in the study. The effects of terpenes on equipment and workplace environment were also examined as part of this project.



1.2 WHAT ARE TERPENES?

Terpenes are a large and diverse class of organic compounds. The word terpene is used both in its broadest sense to designate all compounds which have a distinct architectural and chemical relation to the simple C_5H_8 molecule, and in a more restricted sense to designate compounds with 10 carbon atoms derived from $C_{10}H_{16}$ ($C_{10}H_{16}O$, $C_{10}H_{18}O$) [8]. When terpenes are modified chemically, such as by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally referred to as terpenoids, which contain additional functional groups. In some contexts, the terpenoids are included under the term terpenes but in this report, the term terpenes will only be used for hydrocarbons, i.e. only consisting of carbon and hydrogen.

Monoterpenes result from the combination of two and sesquiterpenes from three branched, unsaturated C5 units (isoprene). In general, the boiling points of the monoterpenes lie between 140 to 180°C, sesquiterpenes lie between 250 and 280°C. The focus of this study is on monoterpenes.

The presence of double bonds in the molecule accounts for the occurrence of isomers. There are structural isomers (which have different sequence of bonded atoms) and stereoisomers (which have the same sequence of bonded atoms but differ in the three-dimensional orientations of their atoms in space).

Classification of terpenes

The terpenes are classified according to the structure of the carbon skeleton and its cyclization type. Most of the terpenes are cyclic except myrcene, Z- β -ocimene and E- β -ocimene which are acyclic terpenes.

Terpenes with a p-menthane skeleton:



Figure 1: p-menthane

These include beyond menthane, α -terpinene, γ -terpinene, α -phellandrene, β -phellandrene, limonene, terpinolene and p-cymene



Bicyclic compounds with carane and thujane skeleton:



Figure 2: Carane (a)and thujane (b)

These include beyond thujane, 3-carene, alpha-thujene, sabinene

Bicyclic compounds with pinane skeleton:



Figure 3: pinane

These include beyond pinanen, α -pinene and β -pinene.

Bicyclic compounds with bornane (camphene) and fenchane skeletons:



a Figure 4: bornane (camphene) (a)and fenchane (b)



b

These include camphene and α -fenchene.

The structure of the terpenes is presented on Figure 5.





Figure 5: structure of terpenes

Among the terpenes,p-cymene and D-limonene have been shown to be of particular importance to biogas plants: p-cymene (C₁₀H₁₄, boiling point 177°C, solubility in water 23 mg/l) is a naturally occurring aromatic organic compound which is classified as an alkylbenzene related to a monoterpene. It occurs naturally in more than 200 food products [8]. p-cymene is mainly ingested by consumption of food products such as butter, carrots, nutmeg, orange juice, oregano, raspberries and lemon oil, and nearly all spices. It is estimated that approximately 30000 kg of p-cymene is consumed every day as a natural element of these food products.

D-limonene ($C_{10}H_{16}$, boiling point 176°C, solubility in water 14 mg/l) occurs naturally in lemon rind, dill, fennel, celery and plants, and in many essential oils. It can also be produced synthetically. D-limonene is frequently used as food additive in order to give a lemon flavor, as a fragrance additive in perfumes, body care products and as natural substitute for petroleum-based solvents in paints and detergents.

1.3 COMPATIBILITY OF RUBBER WITH TERPENES

Rubber materials are used in biogas plants as sealing materials in valves, pipe connections etc. The elastic sealing properties in rubber materials are achieved thanks to the three-dimensional network structure in the rubber molecules.

The chemical compatibility of rubber is extremely important as the rubber can degrade rapidly if the rubber material is not compatible with the environment or media that it comes into contact with. The complexity of the biogas composition makes material selection complicated and tests of the chosen materials may be needed.

Many rubber suppliers propose rubber compatibility chart which rate some rubber materials that come into contact with various chemicals. The data is based on actual service experience, advices of various polymer suppliers and opinion of rubber chemists and often compiled from numerous sources. A rubber compound may swell when exposed to a chemical with similar structure and solubility. The



cross-linked network structure stops the materials to dissolve in the chemical. With a given percent of swell, the function may be satisfactory in a static condition but may fail if the material is subject to for example flexing. The physical properties of the material may also be affected by chemicals. It is also worth noticing that higher temperatures increase the effect of chemicals on rubber compounds. The increase varies with the polymer and the chemical. A compound quite suitable at room temperature might fail very quickly at higher temperatures.

Two examples are presented here; the first one is focusing on hoses [9] (Table 1) and the second one on o-rings [10] (Table 2). The designation for the material is in compliance with ASTM D1418 [11].

ASTM D1418	20°C	D- limonene	p- cymene	pinene	Decahydronaphthalene
CIIR	Chloro- isobutene- isoprene	Х	Х	х	Х
CR	Chloroprene	Х	х	С	Х
CSM	Chloro- sulfonated polyethylene	Х	х	х	х
EPDM	Ethylene- propylene- diene- terpolymer	х	х	х	x
NBR	Nitrile- butadiene	С	Х	С	х
NR	lsoprene Rubber (natural)	Х	х	х	x
SBR	Styrene- butadiene rubber			х	E
UHMWPE	Cross linked polyethylene				E
XLPE	Ultra-high molecular weight polyethylene				E

Table 1: Material compatibility with terpenes, example 1

C: conditional, X: not recommended, Blank: no data, E: Excellent



		Paracymene	Cymene or p- Cymene	Dipentene, limonene	Pinene	Camphene
NBR	Nitrile	Х	4	2	2	2
EPDM	EPDM	х	4	4	4	4
CR	Neoprene	4	4	4	3	4
SBR	SBR	4	4	4	4	4
VMQ	Silicone	Х	4	4	4	Х
IIR	Butyl	4	4	4	4	4
ACM	Polyacrylate	4	4	4	4	4
CSM	Hypalon	4	4	4	4	4
FKM	Viton	1	1	1	1	1
AU, EU	Polyurethane	3	4	4	3	3
FVMQ	Fluorosilicone	2	2	2	2	2
FEPM	Aflas	Х	х	Х	х	Х
FFKM	Kalrez	1	1	1	1	1

Table 2: Material compatibility with terpenes, example 2

1 = Satisfactory, 2 = Fair, 3 = Doubtful, 4 = Unsatisfactory, X = Insufficient Data

The general conclusion that can be obtained from these data is that most of the rubber compounds are not fully compatible with terpenes with the exception of FKM and FFKM. According to the producer, DuPont[™] Kalrez[®] perfluoroelastomer parts (FFKM) resist over 1,800 different chemicals, while offering the high temperature stability of PTFE (327°C). They are used in highly aggressive chemical processing, semiconductor wafer fabrication, pharmaceutical, oil and gas recovery, and aerospace applications. Viton (FKM) is a brand of synthetic rubber and fluoropolymer elastomer commonly used in O-rings, chemical-resistant gloves, and other molded or extruded goods.

However, it is recommended that users conduct their own tests to confirm the suitability of the selected material for each application, taking into consideration factors as the exposure time, the temperature etc.

1.4 WORKPLACE ENVIRONMENT, ODOUR, SENSORY IRRITATION

Chemicals can provoke two types of sensations: the first one being sensations of smell and the second one being sensations of irritancy (typically: burning, tingling or prickling). Sensory irritation involves irritation of the eyes, nose, and throat. Skin irritation is also sometimes included. These two sensations are not necessarily correlated.

For a person to smell something, air containing odoriferous molecules [12] must reach a tiny cluster of specialized nerve cells, the olfactory neurons, well inside the nasal cavity. They are positioned out of the major airstream. Each nasal cavity has about five million of these receptors which are the only nerve cells in the body which have the ability to regenerate. Only a small amount of inhaled air reaches



the odor receptors. The neurons can perceive some 4000 different odors. However, the average person can correctly name only a handful of common odors probably because of an inability to think the name of the substance. Constant exposure to odors can induce non-perception as the neurons become fatigued. People tend to become accustomed to odors even those which they initially find unpleasant.

The minimum concentration of a substance at which a majority of test subjects can detect and identify the characteristic odor of a substance is called Odour Threshold (OT). However, a wide variation in threshold definitions exist.

Measuring OT is a real challenge and seems to result in an apparent lack of consistency from different references. This can be explained by the fact that different methods are used, that the definition varies as well as the sample preparation, the panel selection, the purity of the chemicals and the data interpretation. Moreover, odour threshold is measured essentially for a single chemical with no other chemicals present in the air. Mixtures of different chemicals are even more challenging to study. Mixed chemicals may be totally independent of one another or produce additive or suppressed effects.

Although the sense of smell cannot be relied upon to evaluate the hazards of chemicals, certain odors may result in psychological effects.

So many aspects must be studied when discussing workplace environment.

Workplaces vary greatly in area, shape and volume. However, workplaces can be divided into two general categories: open spaces and confined spaces. Open spaces usually are large areas that have adequate air flow. Confined spaces are spaces with little air flow. Restricted movement of air increases the risk of exposure. In that case, small sources of terpenes become significant because the concentration builds up more rapidly.

The challenge when studying workplaces for exposure to chemicals is to recognize, evaluate and control sources, i.e. identify processes and activities where vapor can be released or dermal exposure can occur.

Exposure of maintenance workers must also be considered. Exposure may arise from terpenes trapped in equipment under repair (risk for dermal exposure) or from emissions produced nearby (inhalation).

Quantitative evaluations of terpene concentrations in different spaces may be performed for a number of reasons, for example: to assess workers' exposure, to determine the need for measures or to assess the effectiveness of control strategies.

The results of quantitative evaluations are usually compared with occupational exposure limits which are typically set by competent national authorities, in Sweden, the Swedish work environment authority (Arbetsmiljöverket). The occupational exposure limit is defined as the highest acceptable average content level of a contaminant in air which is to be inhaled, calculated as a time weighted average, typically during a working day, normally 8 hours (then called level limit value, LLV). The occupational exposure limit, LLV in Sweden is 150 mg/m³ for both total and individual monoterpenes [13].



To assess the exposure of maintenance workers during specific activities, the quantitative evaluations are usually compared to short-term values (STV) set by the same authority. The short-term value is defined as the recommended highest value for exposure calculated as time weighted average over a reference period of 15 minutes. The SVT for terpenes is set to 300 mg/m³.

Monoterpenes [14] have a variety of effects on humans, and the effects depend on their concentrations. At typical ambient concentrations (in and around forests, less than 10 ppb~50 μ g/m³), monoterpenes positively affect humans by reducing stress and fatigue. Inhalation of essential oils containing terpenes increases sleeping time, relieves tension, decreases symptoms associated with anxiety and stress and plays a significant role in regulating the central nervous system. However, at higher concentrations, (>10 ppm~50 mg/m3), monoterpenes caused eye, nose and throat irritation. Wolkoff et al. [15] proposed a human sensory irritation threshold of 3.6 ppm~20 mg/m3 for alpha-pinene and of 79 ppm 440 mg/m3 for limonene. The odour threshold reported in Wolkoff's study was 100 μ g/m³ for α -pinene and 211 μ g/m³ for limonene, much lower than the sensory irritation threshold.

Regarding dermal exposure, monoterpenes are irritating to skin and mucuous membranes and can cause both allergic and nonallergic contact dermatitis [16].



2 Methods

2.1 SAMPLING OCH GAS ANALYSES

2.1.1 Sampling

The gas samples were taken either by operating personnel at the participating plants or by personnel from SP. In both cases, gas was sampled in gas sampling bags of type Altef and on an adsorbent, Tenax, with a controlled flow over a short period (1-2 minutes). Samples were collected before (biogas) and after upgrading (biomethane). In total, 8 different plants participated in this study.

2.1.2 Gas analysis

The analyses were performed on a gas chromatograph (Agilent technologies 6890N) equipped with a flame ionization detector and a mass spectrometer 5975C inert MSD in the so-called electron impact mode. The GC column was a non-polar capillary column (5% phenyl polysilphenylene-siloxane, BPX5, 50 m long, 0.32 mm internal diameter, 1 µm film thickness). The desorption of the Tenax tubes were carried out on a Markes TD100 desorbed, where the adsorbed substances were released by heating the sorbent tubes during 7 min at 275°C and then transferred to a cold trap for focusing. The trap was then rapidly heated up again and terpenes were released and reached a gas chromatography (GC) column for separation. The column effluent was split into two streams for the detection of individual compounds, one stream passing through the flame ionization detector and the other stream through the mass spectrometer. Terpenes were quantified by means of an external calibration curve (response ratio versus amount ratio) obtained from the FID signal.

2.1.3 Calibration and determination of the retention time

To ensure the correct identification of the terpenes studied and a good chromatographic separation, the retention time for each terpene was determined by analyzing all targeted compounds individually in solution at 200 ng/µl. Several dilutions were also performed for calibration purpose. Overlaid chromatograms are shown in Figure 6. A reasonable separation was achieved even if p-cymene (g) and D-limonene (h) are eluted quite close to each other.

2.1.4 Test of the method

The trapping efficiency on Tenax TA of terpenes present in gas samples was tested by preparing a gas containing terpenes at known concentrations. An ALTEF gastight bag (Restek, Bellefonte, Pennsylvania, USA) filled with methane was spiked with terpenes so the concentration in the gas was 75 mg/m³ for p-cymene, 45 mg/m³ for D-limonene, 18 mg/m³ for α -pinene, 9 mg/m³ for camphene, β -myrcene, β -pinene, α -terpinene , γ -terpinene, 1 mg/m³ for eucalyptol and 3-carene. These concentrations were chosen as they are representative of concentrations found in real biogas samples. 100 ml of the gas was then sampled onto a Tenax tube, directly (t = 0 hours) using a pump. The experiment is repeated after 5 hours and



after 120 hours storage in the bag. The recovery yields expressed as the ratio between the measured concentration and the targeted concentration was then calculated.

The results show that the terpenes are quantitatively recovered on Tenax tubes (recovery > 85%). A slightly lower recovery yield was observed for p-cymene and D-limonene at t=0 and is probably due to adsorption effects on the wall of the bag as these two compounds are at higher concentrations than the other terpenes. The terpenes' concentrations decrease at t = 120 hours for most of the tested compounds probably due to time dependent adsorption effects.



Abundance

Figure 6: overlaid chromatograms of a: α -pinene, b: camphene, c: β -myrcene, d: β -pinene, e: 3-carene, f: α -terpinene, g: p-cymene, h: D-limonene, i: eucalyptol, j: γ -terpinene

2.2 BMP TEST

In order to perform a mass balance and to investigate the influence of the substrate composition and the digester temperature on the amount of terpenes in the biogas under controlled conditions two sets of batch tests were set up. The tests were set up as biochemical methane potential (BMP) tests following the protocol suggested by Angelidaki *et al.* [17] with the exception that no nutrient/buffer media was used and pure nitrogen gas was used as flushing gas. Inoculum for the tests were collected from two different biogas plants treating mixed substrate with a high degree of food waste – one running at mesophilic and one at thermophilic temperature.

The substrate was a mixture of different substrates with a high degree of food waste collected from the mesophilic plant. The tests were performed on two different occasions. For the first test, the substrate was collected in May (after the winter period, high consumption of citrus fruits) and for the second test, the substrate was collected in September (after the summer period, the low consumption of citrus fruits).



A spiked substrate was also produced by adding finely ground outer layer of orange peel (11.5 g to 3 kg of substrate).

Controls were prepared containing only inoculum and tap water and the activity of the inoculum was tested with microgranular cellulose (Sigma-Aldrich C6413). The inoculum to substrate ratio was 2 to 1 on a VS basis and in the first test, the loaded substrate concentration was 3.5 g VS/L after dilution with tap water and 200 ml of substrate/inoculum/water mixture was added to 245 ml gas tight test bottles. As the concentrations of terpenes were found to be on the upper limit of what can be analyzed with an acceptable uncertainty, in the second test, it was decided to produce significantly lower volumes of biogas than in the first test by reducing the loaded substrate concentration to 0.9 g VS/L (dilution with tap water) and adding only 80 ml of substrate/inoculum/water mixture to the bottles The substrate/inoculum/water mixture was added to 245 ml gas tight test bottles. The head space was purged with nitrogen after which the bottles were sealed and incubated at 37°C and 55°C respectively. Blanks, controls and tests were performed with six replicates. Three of the replicates were equipped with needles connected to a Tenax tube (adsorbent) and then connected to a gas sampling bag of type Altef. The terpenes were then quantified as described in section 2.4.2. The remaining three replicates were used to follow the gas production by gas chromatography as described by Angelidaki et al. [17]. The gas chromatograph used was a Perkin Elmer Clarus 480 with a packed column (2.5 m, 3.2 mm, Porapak, 50-80 mesh), with helium as the carrier gas and equipped with a thermal conductivity detector. The injector temperature was 80°C, column temperature 60°C and detector temperature 150 °C. Samples of 0.2 ml were collected regularly from the headspace of the BMP bottles with a gas tight syringe and the peak areas of the over-pressurized samples were related to those of a 0.2 ml sample of a standard gas mixture (75 % CH4, 15 % CO2 and 10 % N2) collected at atmospheric pressure. The total volume in the headspace at the time of sampling was then calculated. Gas production from the inoculum was subtracted from the total gas production in the test bottles in order to calculate the BMP, which was expressed as the cumulative amount of methane produced in STP conditions (0°C, 1atm) after a plateau in methane production was reached (after 30 days) relative to the amount of VS introduced.

2.3 EXPOSURE TEST

In this investigation two rubber materials were selected for investigation, Nitrile Butadiene Rubber (NBR) and Epichlorohydrine Rubber (ECO).

NBR consists of the two monomers Acrylonitrile and Butadiene (Fig 7). The properties of the final material are dependent on the composition of the two monomers and other additives. The rubber polymer is generally mixed with carbon black and other fillers, stabilizers crosslinking agents etc. in order to achieve the final product with desired properties. The cross-linking reactions (vulcanization) take place at the double bonds on the polymer molecule. Generally, NBR is resistant to aliphatic hydrocarbons, but can be attacked by ozone, ketones, esters and aldehydes. See more information about chemical resistance of rubber materials in Tables 1 and 2.





Figure 7. Structure of NBR rubber

Epichlorohydrin rubber (ECO) has better low temperature flexibility compared to NBR and is resistant to acids, alkalis and ozone. The resistance to aldehydes is poor.

The two types of sealing rings were exposed to gaseous terpenes at 100°C for four weeks. Each of the rubber type was placed in a desiccator and sealed. In order to simulate a biogas approximately 1 ml of the two most commonly found terpenes i.e. D-limonene and p-cymene was added at the bottom of the desiccator. The desiccators were then put in a heating cabinet at 100°C. This rather long exposure at elevated temperature causes both physical changes to the material and some degradation. The gas concentration was measured at the end of the test period to ensure that the desiccators were gas tight and the rubbers had been exposed to the terpenes. Gas was withdrawn through Tenax tubes using a syringe. The tubes were analysed as explained in the section 2.4.2 of this report.

In a biogas plant the materials may also be exposed to terpenes in condensed phase (condensate). Therefore, samples were also exposed to a water solution of terpenes at room temperature for a week according to ISO 1817 [18]. The exposure media was a water solution of condensed raw gas from two different biogas plants. Swelling is mostly a physical effect on the material. A week of exposure is therefore enough to evaluate if the exposure media affects the rubber.

In order to evaluate changes in the rubber properties, hardness and volume change were measured.

Hardness was evaluated according to ISO 48 on a Bareiss Digitest hardness tester. An indentor is applied on a flat rubber surface and the penetration depth is measured. Volume change was measured by weighing the samples in air and water and calculating the volume according to Archimedes principle.

2.4 WORKPLACE

In order to evaluate potential exposures to terpenes at biogas plants, field measurements and analyses were conducted. The sampling points were identified from a form that was sent to operational technicians at 3 biogas plants. The following questions were asked:



Table 3: Questions to plants regarding workplace environment

In which place may the personal be exposed to terpenes? (specify how long time per day, if the ventilation is good in this place, Describe the odour, strength/intensity and character)

What do you see as your biggest health or safety problem which may be related to terpenes?

Are there specific tasks in which you are exposed (or suspect that you are exposed) for direct contact (breathing or skin contact) with terpenes? How often do you perform the above tasks and for how long time?

Do you have at your workplace any special protection today to avoid exposure to terpenes? Ex protective breathing equipment, gloves, etc.

Are the rooms / areas where the raw gas or condensate may be released in any way? (Specify how long time per day, if the ventilation is good in this place, how is the experienced odour? Describe the odour, strength/intensity and character)

Sampling of terpenes was performed by active sampling on Tenax adsorbent tubes using a pump. Two adsorbent lines in parallel were used, using two different sampling flows, for example, 20 and 50 ml/min. Each had a backup sampling tube also containing Tenax to collect any breakthrough.

2.5 SUBSTRATE ANALYSES

Biogas substrate is a complex matrix composed of a great variety of organic compounds. A crucial step of sample preparation is the isolation and enrichment of the compounds of interest. Samples of homogenized and hygienized substrate from biogas plants where food waste are digested were collected in plastic bottles and sent directly to the laboratory where they were placed in the freeze until analysis.

About 100 g of substrate collected at the biogas plant were mixed in a mixer for homogenization. About 10 g of the mixed substrate is then introduced in 500 ml water. A measured amount of sample (9 ml) is placed in a sealed vessel. The sample is purged with an inert gas (N₂), causing VOCs including terpenes to be swept out of the sample. The VOCs are retained in an analytical trap (here a Tenax tube), which allows the purge gas to pass. The VOCs are then thermally desorbed, and separated and detected by GC/MS. There are many factors that affect the efficiency of this extraction. The amount of each compound purged is proportional to both its vapor pressure and its solubility in the sample. Both of these are in turn, affected by the sample temperature.

One substrate was chosen to determine the time required for quantitative extraction. The concentration of D-limonene was found to be stable at 50 ppm w/w (50 μ g/g) when bubbling 30 minutes or longer time. However, when bubbling shorter time as 5 min or 15 min, the concentration of D-limonene was found to be lower; indicating that the extraction was less efficient with these extraction times.

The efficiency of the purging process was also verified by performing a second purge. Less than 10% of the compounds totally purged were found in the second purge showing that the first purge has an efficiency of >90%.



3 Results

3.1 SUBSTRATE

Abundance

The results of the analyses performed on the substrates collected at different plants show that D-limonene is one of the dominant VOC purged of the substrate as it can be seen as it can be seen on Figures 8 - 10 (Plant 1 to 3). Other VOCs purged are linear esters with an ethyl or propyl group attached to the oxygen atom in the chain of an ester molecule having between 6 to 14 carbon atoms.

On the other hand, p-cymene is found to be the dominant terpene in the digestates studied as it can be seen on Figure 11.

However, with this method, it was proven difficult to obtain reproducible results and many tests failed (incoherent results were obtained). We only present the results where the reproducibility between triplicates was acceptable. Even if Tenax TA has a low affinity for water, it seems that the adsorption of VOC was sometimes not efficient due to the high water content.



Figure 8: GC chromatogram of substrate at plant 1





Figure 9: GC chromatogram of substrate at plant 2



Figure 10: GC chromatogram of substrate at plant 3





Figure 11: GC chromatogram of a digestate

The distribution of terpenes found in the substrate is shown in the figure 12



Distribution of terpenes in the substrate at 4 different plants (food waste: 25 to 85 %)

Figure 12: Distribution of terpenes in the substrate at 4 different plants digested 25 to 85% food waste



The average distribution of terpenes is as follows:

- D-limonene, 91 to 94%
- p-cymene. 1%
- beta-myrcene: 1-2%
- alfa-pinen: 1 %
- gamma-terpinene: 2%

D-limonene is clearly the dominant terpene in the substrates studied here. In all cases, D-limonene represents more than 90% of all terpenes found in the substrates. P-cymene represents 1% whereas beta-myrcene and gamma-terpinene represents each 1-2% of the terpenes.

On the other hand, p-cymene is found to be the dominant terpene in the digestates studied. P-cymene represents more than 90% of all terpenes found in the digestates.

As p-cymene was found to be largely predominant in the digestate, it can be assumed that a reaction converting D-limonene into p-cymene occurs within the biogas production. In a thermophilic process where the temperature is higher (55°C), a higher amount of D-limonene may evaporate in the biogas compared to a mesophilic process (35°C) where D-limonene is to a higher extend converted to p-cymene which evaporate in the biogas. At the one plant (plant 5, figure 13) with mesophilic process where D-limonene is the predominant terpene, one can assume that constituent helping catalyzing the conversion of D-limonene into p-cymene is missing explaining the present of D-limonene in the biogas. This plant is the only plant in this study, co-digesting waste water sludge; it would be interesting to investigate if there is a possible effect due to this other substrate. Another plant, which was not participating in the study and which also co-digests food waste and waste water sludge shows the same trend regarding the composition of the gas with regard to terpenes.

The theoretical value was calculated according to different scenarios (concentration of orange peel in the substrate varying between 5 to 15%, proportion of food waste in the substrate varying from 25 to 80%, D-limonene concentration in orange peels varying from 5 mg/g to 10 mg/g). About 70% of the oranges produced are transformed into juice, marmalade and other foods, leading to the production of an amount of citrus peel waste that represents about 50-60% of the processed fruit [19]. D-limonene concentration in the substrate varies from 50 µg D-limonene/g substrate up to 1200 µg D-limonene/g substrate.

The results are presented in the Table 4.



Proportion of orange peel in the substrate*	D-limonene in orange peel**	Proportion of food waste in the susbtrate***	D-limonene in the substrate
%	mg/g	%	µg/g
15	10	80	1200
15	5	80	600
10	10	80	800
10	5	80	400
5	10	80	400
5	5	80	200
15	10	50	750
15	5	50	375
10	10	50	500
10	5	50	250
5	10	50	250
5	5	50	125
15	10	20	300
15	5	20	150
10	10	20	200
10	5	20	100
5	10	20	100
5	5	20	50

Table 4: Theoretical calculation of D-limonene concentration in substrate according to different scenario

*[20]

**[21]

*** Information provided by the participating plants

The theoretical amount of D-limonene in a substrate varies from 1200 μ g D-limonene / g substrate to 50 μ g D-limonene / g substrate.

As reported above, D-limonene concentration found in a substrate containing 20% of food waste was 50 μ g/g which is coherent with the theoretical value but in the lowest range (with most of the scenarios, the concentration of D-limonene is higher than 50 μ g/g). This can be explained if a proportion of D-limonene present in the substrate cannot be purged.

3.2 BIOGAS AND UPGRADED BIOGAS

Biogas:

Samples of biogas were collected at 8 different plants (3 having thermophilic process and 5 having mesophilic process). The samples were collected in the months of April or May. The concentration of terpenes in the biogas is presented in Figure 13 for the 4 terpenes that were found to be dominant in these samples. As it can be seen on this figure, p-cymene is clearly dominant in the biogas produced during a mesophilic digestion with an obvious exception for plant 5 where D-





limonene is clearly dominant. On the contrary, the ratio D-limonene/p-cymene is found to be more balanced when the biogas is produced by a thermophilic process.

Figure 13: Concentration of terpenes in biogases at 8 different plants (5 mesophilic and 3 thermophilic).

The sum of terpenes in the biogas was then plotted against the proportion of food waste in the substrate at theses 8 plants. There is a linear positive correlation between the amount of food waste digested in the substrate and the amount of terpenes found in the biogas up to 70%. (Figure 14). When the amount of food waste in the substrate is high (>70%), the concentration of terpenes in the biogas seems to level out.





Sum terpenes / proportion of food waste in the substrate

Figure 14: Concentration of terpenes in biogases versus proportion of food waste in the substrate

At 3 selected plants, samples of biogas were analyzed on 3 different occasions: April, August, and November. The results are presented in Figure 15. The concentrations of terpenes seem to follow seasonal variations, mostly at the plants using a mesophilic process.



Concentration of terpenes in biogas

Figure 15: Concentration of terpenes in biogases at 3 different occasions at 3 plants





This trend has been compared to the import of citrus fruits over a year which we assumed is directly correlated to their consumption (Figure 16).

Figure 16: Import of citrus fruits over a year

Taking into account the retention time of the anaerobic digestion, the 3 occasions correspond to:

- Sampling in April: end of the period with high consumption of citrus fruit: The concentration of terpenes in the biogas is high.
- Sampling in August: during the period of low consumption of citrus fruits: The concentration of terpenes in biogases is much lower than during the previous sampling campaign.
- Sampling in November: beginning of the period with high consumption of citrus fruits, the concentration of terpenes in the biogas increases again at the plants with mesophilic process.

However, it is important to note that the base (n = 3 plants, n = 3 sampling occasions) is small. It would be interesting to reproduce a similar study on a larger base (sampling every month during 1 year in at least 5 different plants).

Biomethane

Samples of biogas and biomethane were analyzed at 7of the plants, 3 using an amine scrubber, 3 using a water scrubber and 1 using PSA as upgrading techniques. The results of the biomethane analyses are presented on Figure 17.





Concentration of terpenes in biomethane

Figure 17: Concentration of terpenes in biomethane

The concentration of terpenes in the biomethane varies from 240 mg/m³ down to 5 mg/m³. The removal efficiency (representing the percent of terpenes that have been removed from the biogas) of the different techniques was calculated to be as follows:

- Water scrubber: 96%, 83%, 95%
- PSA: close to 100%
- Amina scrubber: 71%, 85%, 61%

Despite the small base, these results can be compared to results obtained during a previous study [22] where the removal efficiency for VOC in biogas using different upgrading techniques was measured at 11 plants. In the previous study, PSA was also found to be very effective technique (concentrations of VOC in the biomethane 5 mg/m^3 and 3 mg/m^3). The results obtained during the previous study for water scrubber upgrading plants is also comparable to the results obtained here. However, the results obtained with amine scrubbers slightly differ in the 2 studies. In the previous study, only small amounts of VOCs were recovered in the biomethane when upgrading with amine scrubber (typically 10 mg/m³). The biogas was collected at waste water treatment plants or was a combination of biogas produced from food waste and from waste water treatment sludge. Not only terpenes were present in the biogas, but also other hydrocarbons (as toluene, decane etc...). In this current study, the amounts of VOCs (=terpenes in this case) in the biomethane is found to be significantly higher (240, 180 and 125 mg/m³). In the previous study, it was shown that VOCs are removed during the drying step and not during the removal of carbon dioxide.

A hypothesis to explain the difference between the two studies is that in the current study, at the amine scrubber plants tested, the temperature of the gas is not reduced to 5°C as it is the case for larger amine scrubber units. If the temperature of the gas is lower, the terpenes will to a greater extend follow the condensate.



3.3 BMP TEST

The results of terpene analyses in the biogas produced from substrate in the batch tests are presented in Figures 18 and 19 (only D-limonene and p-cymene are presented since these were clearly dominant). The production from the blank test has been subtracted and the results have been normalized with respect to the mass of added substrate. The production of terpenes in the first test was on the upper limit of what can be analyzed with acceptable uncertainty and therefore the second test was designed to produce significantly less biogas. In some cases, the production in the first test may have been underestimated. In cases where individual results were significantly lower than the other replicates these were excluded before calculating the average. However, the produced amounts of terpenes in the second test are significantly lower per added amount of substrate, which indicates that there are less terpenes in the substrate used in this test.



Figure 18: Mass of D-limonene and p-cymene in biogas in the first batch tests. The production from blank has been subtracted and the results have been normalized with respect to the mass of added substrate (ng terpenes / g substrate).





Figure 19: Mass of D-limonene and p-cymene in biogas in the second batch tests. The production from blank has been subtracted and the results have been normalized with respect to the mass of added substrate (ng terpenes / g substrate)

The distribution of p-cymene and D-limonene obtained in the different tests are presented in Table 5. Even if the substrate's composition may differ in both tests, the same trend was observed; D-limonene is clearly the dominant terpene in thermophilic processes while a mixture of D-limonene and p-cymene is found in mesophilic processes.

	Test 1 (May)		Test 2 (Se	eptember)
	D-limonene p-cymene		D-limonene	p-cymene
Mesophilic test	40%	60%	40%	60%
Thermophilic test	80%	20%	100%	0%
Mesophilic test with spiked substrate	65%	35%	60%	40%
Thermophilic test with spiked substrate	85%	15%	100%	0%

Table 5: Distribution between D-limonene and p-cymene in the different BMP tests performed

The BMP for the substrate mixtures tested was 800-900 NL CH_4/kg VS for both tests. No significant difference was observed for the spiked substrate.

An attempt to perform a mass balance (in μ g) for D-limonene (D-limonene in the biogas, D-limonene in the substrate) based on the results from the batch test 1 is shown in Table 6 for a substrate containing 20% food waste and the substrate spiked with the out layer of orange peels (added about 5% D-limonene to the substrate).



μg	Mesophilic		Thermophilic	
	Substrate	Spiked substrate	Substrate	Spiked substrate
Terpenes in the gas	75	208	60	195
Terpenes in the substrate	491	511	491	511
Terpenes substrate/terpenes gas	6,5	2,5	8,2	2,6
D-limonene in the gas	29	125	43	157
D-limonene in the substrate	470	489	470	489
D-limonene substrate/D- limonene gas	16,2	3,9	10,9	3,1
p-cymene in the gas	40	71	11	28
p-cymene in the substrate	4,7	4,7	4,7	4,7
p-cymene substrate/p- cymene gas	0,1	0,1	0,4	0,2

Table 6: Batch test results showing terpenes concentrations in gas and substrate

*measurement failed

The results show that the amount of D-limonene is 6 to 8 times higher in the substrate than in the gas. Another possible explanation for this relatively low value is that part of the terpenes is further degraded to methane.

However, just added a small portion of orange peels to the substrate provokes a noticeable increase of the concentration of D-limonene in the gas. The hypothesis is that D-limonene is strongly absorbed in the substrate, while in the added orange peel it may be more easily released. This is probably due to the strong affinity between the organic matter from the substrate and the hydrophobic D-limonene. However, the increase is un-proportionally high which may be due to uncertainties in the analysis of terpenes in the substrate. In all cases, the concentration of p-cymene is much higher in the gas than in the substrate showing that this compound is formed in the reactor.

Calabro *et al.* [23] have proposed a pathway for the bio-conversion of D-limonene to p-cymene. D-limonene is initially protonated before being subject to Meerwein-Wagner 1-3 hydride shift to form the cations of α - and β -phellandrene (catalytic reaction). These are then very quickly biologically dehydrogenated to p-cymene.

3.4 EXPOSURE TEST

The results of the tests performed on the two tested materials are presented in Tables 7-8.

Table 7 Material properties after four weeks at 100°C in an environment containing gaseous terpenes

Material	Hardness change (%)	Volume change (%)	
NBR	26	-0,3	
Epichlorohydrin	-0,6	-0,6	



Material	Hardness change (%)	Volume change (%)	
NBR	-7,4	0,5	
Epichlorohydrin	-21,6	5,3	

Table 8 Material properties after one week at room temperature in raw gas condensate

A high value on the hardness indicates a harder material and a low value a softer material. Hardness is dependent on the degree of cross-linking or vulcanization, amount of filler and plasticizers or degradation of the material. A high degree of cross links and high amount of filler makes the material harder while plasticizer makes it softer. Type and composition of the rubber polymer also affect the hardness. Degradation of the material may alter the hardness. Depending on the degradation mechanism the hardness may either increase or decrease upon chemical ageing. Absorption of liquids generally makes rubber materials softer while plasticizer extraction makes the materials harder.

The exposure in gaseous terpenes did not affect the volume of the materials to any great extent. The NBR became much harder after the exposure, the hardness increased from 66 IRHD (International Rubber Hardness Degrees) to 83 IRHD after the exposure. This increase is most probably a degradation effect since the volume was not affected by the exposure.

Both materials were significantly affected by the condensed raw gas and both of them absorbed the liquid and became softer, i.e. had a lower value of hardness after exposure. The Epichlorohydrin rubber was more affected than the NBR rubber.

It should be pointed out that the condensed liquid contains a number of different species, not only terpenes and therefore it is not possible to draw any further conclusions about what causes the observed effect. Neither do we know anything about the rubber formulation except for the type of rubber polymer.

The gas in the desiccators was analyzed at the end of the test period to ensure that the rubbers had been exposed to the terpenes. Apart from terpenes, many compounds were found to be present in the desiccator. In order to determine if the release of these compounds from the rubber was due to exposure to terpenes, the gas composition was compared to the gas inside desiccators where rubbers were not exposed to terpenes but only heated in a cabinet at 100°C.



The results are presented in Figures 20 - 21.





Abundance



Figure 21: Compounds being released from Epichlorohydrin while warmed at 100°C

The same compounds were identified in the desiccators where rubbers were exposed to terpenes but in higher amounts (the analyses were only semiquantitative).



3.5 WORKPLACE

The answers from the operational technicians clearly identified the upgrading plant as the place to assess potential exposures to terpenes. In normal drift and with the exception of specific work tasks, the digestion process takes place in sealed tanks. However, when the gas is upgraded to vehicle fuel quality, water present in the biogas must be removed. The largest proportion of this process water is recirculated but a portion of the water is regularly removed. The amount of this water depends on the upgrading process. In some plants, the process water is collected in a well before being sent to the recipient. Terpenes have low water solubility so if the terpenes are at high concentrations in the water, the terpenes will gather at the top of the water in an oily insoluble layer. The upgrading plant often consists of several rooms where different processes occur.

Operational technicians identified headache occurring when personal stay longer time in some places as the biggest health or safety problem related to terpenes. Even the occurrence of strong unpleasant odors (described as oily or citrus odor) was reported. Sampling points for occupational exposure tests were identified based on the following criteria: locations normally occupied by employees, such as the control room of the upgrading plant and the rooms directly connected to this room and the high-pressure compressor rooms (where the gas is pressurized to 250 bar). A confined space (a small WC-room connected to the control room of the upgrading plant) was also identify at one plant.

In addition to the air sampling for occupational exposures, the level of terpenes was measured during specific activities: real-time exposure of a worker performing a change of particle filter (upgrading plant) and drain of the high-pressure compressor oil (compressor station) was studied. The tubes were placed in the worker's breathing zone.

The results for concentration measurements are shown in table 9.



Table 9: Concentrations of terpenes in workplace environment

Sampling point	Description	Date	Compounds	Conc (mg/m ³)
Occupational	High-pressure compressors	19/8	D-limonene	1,5
exposure	room:		p-cymene	18
	outside of this room, there is a well for stormwater where a part of the process water is also collected. The odour outside and inside this room is described as very strong		All terpenes	21
Occupational	Control room of the upgrading	15/9	D-limonene	1,8
exposure	plant: in this place, the technicians can work several		p-cymene	0,1
	hours in a row. A window has an oily coating, the door has turned yellow. Strong citrus odour		All terpenes	2,0
Occupational exposure	CO2-room: Connected directly to	15/9	D-limonene	0,5
	the control room above.		p-cymene	< 0,1
			All terpenes	0,5
Confined space	Small space (WC-room) outside the control rum Strong odour, the surfaces of the room are coated with a yellow layer. The odour is described as citrus /unpleasant	15/9	D-limonene	18
			p-cymene	0,6
			All terpenes	19
Confined space	Small space (WC-room) outside	25/4	D-limonene	690
	the control rum		p-cymene	2
	room are coated with a yellow layer. The odour is described as citrus /unpleasant		All terpenes	700
Specific activities	Replacement of a particle filter	27/5	D-limonene	3,5
	for biogas to be upgraded. During theoperations water is released		p-cymene	8
	and the odour is described as very strong		All terpenes	12
Specific activities	Drain of the high-presure	17/8	D-limonene	2,3
	compressor oil in the compressor		p-cymene	2,2
			All terpenes	5

Logically, the distribution of terpenes identified at the sampling points to assess potential exposures to terpenes mirrors the distribution of terpenes in the biogas at the different plants (Figure 22). The major terpenes detected were D-limonene and pcymene. The workplaces showed low terpene concentrations of max 20 mg/m3. Monoterpene concentrations in the vicinity of workers performing different tasks were quite low and in each case much lower than both LLV (300 mg/m3) and SVT (150 mg/m3). However, the concentration of terpenes was found to be higher than SVT in a confined space at one plant. The presence of an oily yellow coating on the surfaces of this room suggests that high concentrations of terpenes have been released.





Figure 22: Distribution of terpenes (D-limonene, p-cymene, other terpenes) in workplace samples versus terpenes in biogas samples

However, all these concentrations are much higher than the reported odor threshold for terpenes (13 ppb~0,07 mg/m³ (fruit and vegetable flavor, recent advances and future prospects), 40 ppb~0.2 mg/m³ (triangle method).



4 Conclusions

4.1 **OBSERVATIONS**

There is a linear positive correlation between the amount of food waste digested in the substrate and the amount of terpenes found in the biogas up to 70%. When the amount of food waste in the substrate is high (>70%), the concentration of terpenes in the biogas seems to level out. The concentration of terpenes found in this study varies from 360 mg/m³ up to 1650 mg/m³. Significant variations of the concentration of terpenes in biogas were observed when sampling at the same plant at 3 different occasions.

P-cymene is clearly dominant in the biogas produced during a mesophilic digestion with one obvious exception where D-limonene is clearly dominant. On the contrary, the ratio D-limonene/p-cymene is found to be more balanced when the biogas is produced by a thermophilic process

D-limonene is clearly the dominant terpene in the substrates representing more than 90% of all terpenes.

On the other hand, p-cymene is found to be the dominant terpene in the digestates, representing more than 90% of all terpenes.

The concentration of terpenes in the biomethane varies from 240 mg/m³ down to 5 mg/m³. The removal efficiency (representing the percent of terpenes that have been removed from the biogas) of the different biogas upgrading techniques was calculated to be:

- Water scrubber: 96%, 83%, 95%
- PSA: close to 100%
- Amine scrubber: 71%, 85%, 61%

It is worth to notice that only smaller scale amine scrubbers were tested in this study. With larger amine scrubber units, the gas is usually cooled down to 5°C in a gas pretreatment step and the removal efficiency will most certainly be comparable to the removal efficiency from the other techniques.

A possible dependency between the concentration of terpenes in the biogas and the consumption of citrus fruits is proposed based on the results obtained while sampling and analyzing at 3 different occasions at 3 plants. This needs to be verified with a larger base (possibly sampling every months during 1 year in at least 5 different plants).

4.2 CONCLUSIONS

Based on the observations made during this study, it is supposed that terpenes enter the biogas plants as D-limonene present in the substrate, probably mostly originating from citrus fruits for which wastes represent about 50-60% of the processed fruit. In a mesophilic process, it seems that most of the D-limonene is converted to p-cymene inside the substrate whereas in a thermophilic process, some of D-limonene evaporates to the biogas before the conversion. This different



behavior can be explained by the differences in temperature and in microorganisms' population (having different properties). There is one noticeable exception in a mesophilic process where the conversion didn't occur probably due to the presence or absence of other substances. This phenomenon was also observed somewhere else and both times, food wastes were digested together with waste water treatment sludge. However, more tests must be conducted in order to reach a conclusion.

The proportion of terpenes in the gas is proportional to the proportion of food wastes in the substrate independently of the process (mesophilic or thermophilic) up to about 70%. When the amount of food waste in the substrate is high (>70%), the concentration of terpenes in the biogas seems to level out. The concentration of terpenes in the substrate varies over a year probably correlated to the consumption of citrus fruits.

Results obtained from the batch tests suggest that D-limonene is either strongly absorbed in the substrate, (as only about 12-15% the D-limonene present in the substrate was recovered in the biogas as D-limonene, p-cymene...) or further degraded to methane (possibly after the conversion to p-cymene).

Most of the terpenes from the biogas will be recovered in the process water as the upgrading t techniques often efficiently remove terpenes (efficiency between 60 to 100%).

Rubber materials studied here were shown to be affected in a terpene environment (mostly when exposed to condensate containing terpenes).

The high concentration of terpenes found in biogases (360 mg/m³ up to 1650 mg/m³), upgraded gases (5 to 240 mg/m³), water samples (20 mg/L) and workplaces (some mg/m³ up to 700 mg/m³) can lead to condensation of terpenes at the locations where the physical conditions (temperature and/or pressure) change. If terpenes condensate and as they are not soluble in water, an oily layer may be formed.



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TERPENES IN BIOGAS PLANTS DIGESTING FOOD WASTES

Food waste contains so-called terpenes, a group of volatile compounds which originate from among other citrus fruits. These substances result in bad odor and may lead to health issues for workers at the biogas plants as well as result in process design challenges in the production of biogas and biomethane.

This report gives an overview of the content of terpenes in food waste as well as the path of these terpenes in the digestion process. The study shows that the concentrations in substrate, biogas and digestate are higher in the digestion of food waste than in biogas from other substrates, and that the concentration varies over the year. The concentration of terpenes in the biogas plants investigated was usually below the limit for serious health problems, but interviews with technicians at the plants have shown that bad odor and headache are common.

D-limonene is the most abundant terpene in food waste. This is partly transformed to p-cymene dependent on the digestion process. Both thermofile and mesophile digestion has been investigated in this study. Although biogas from food waste shows higher concentrations of terpenes than biogas from other substrates, the largest amount of terpenes is found in liquid condensate. When the biogas is upgraded to biomethane, almost all of the terpenes are removed within the upgrading process.

Terpenes have in this study been shown to have a weakening effect on rubber material which are commonly used in seals, and that this effect is most dominant when the rubber is in contact with terpenes in liquid (i.e. condensate). Knowledge of terpenes in the biogas digestion process is therefore of great importance for the choosing of materials in process equipment.

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