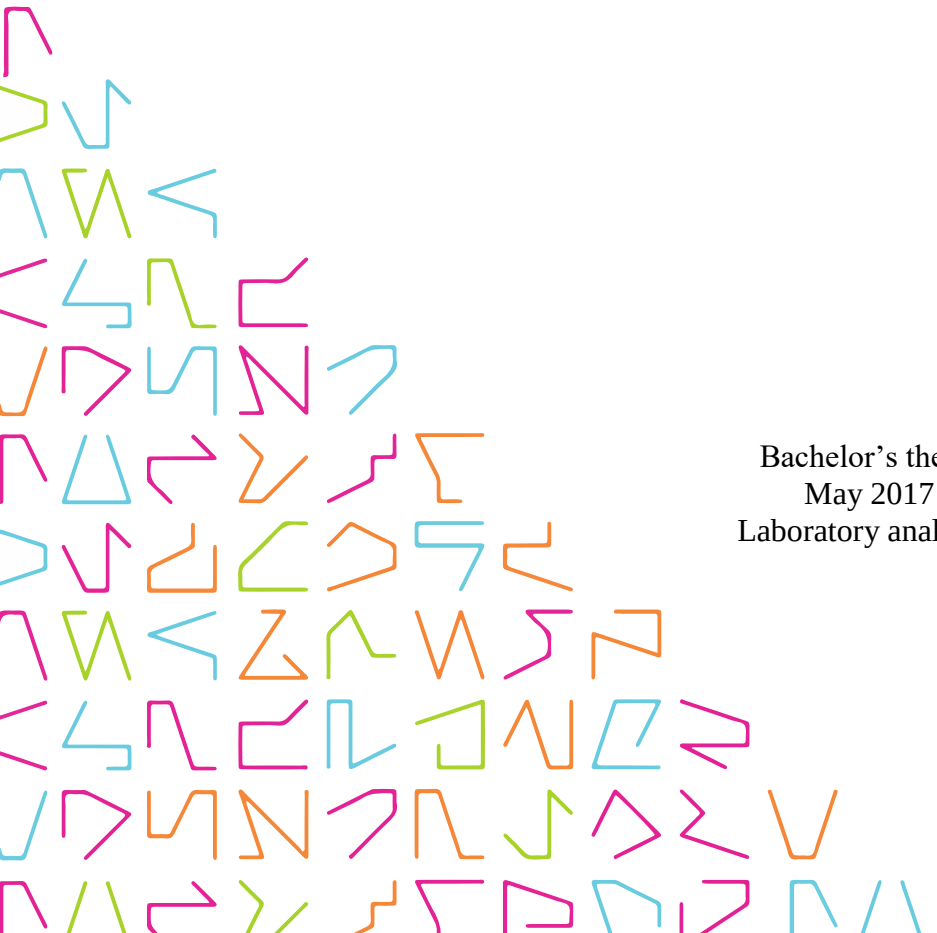
TAMPERE UNIVERSITY
OF APPLIED SCIENCES

Method development for quantitative analysis of methanol and furfural with GC-MS-headspace

Juho Soininen



Bachelor's thesis
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ABSTRACT

Tampereen ammattikorkeakoulu
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Laboratory analytics

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Method development for quantitative analysis of methanol and furfural with GC-MS-headspace

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As part of a project of Tampere University of Technology (TUT) a method was required that could be used to analyze methanol and furfural in torrefaction condensate. The torrefaction condensate is a byproduct of the torrefaction process and has no real energy value itself. The goal of the project was to determine whether the condensate could be used as a growth feed for microalgae to make their growth more efficient. This condensate contains methanol and furfural, which are beneficial to microalgae. But the condensate is highly acidic and as such cannot be used without some pretreatment. For the purposes of analyzing the effectiveness of these pretreatments a new analysis method was required. The method would be used to determine how well these pretreatments removed acids without impacting the concentrations of methanol and furfural too much.

The method was developed for gas chromatograph mass spectrometer with a headspace sampler since it could be used to both quantify and qualify compounds in the condensate. The primary parameters that were optimized in the method were for the gas chromatograph, such as the temperature program. This was done as thanks to the fact that headspace-analysis uses the natural evaporation of compounds to its advantage and as such sample preparation is much simpler. The primary thing to watch out for was to ensure that the samples were diluted enough to prevent saturation. The parameters for the GC were optimized so that the peaks in the chromatograms weren’t overlapping or the run cutting off before relevant compounds can be identified. In addition to the programming, research was done on trying to optimize the method so that it could be used to analyze acetic acid as well. This was done since the condensate contained high concentrations of it. The effects of sample salting and adjustment of the parameters of the headspace sampler were studied as well as a means of improving the accuracy of the method.

The parameters were checked and optimized so that the result was a method that could be used to quantify methanol and furfural accurately. There are also, due to the salting tests, options on how to implement the method.

Key words: Headspace, Torrefaction, Bio-energy, Pyrolysis

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JUHO SOININEN:
Menetelmän kehitys furfuraalin ja metanolin kvantitatiiviseen analyysiin GC-MS headspace-laitteella

Opinnäytetyö 27 sivua, liitteet 2 sivua
Elokuu 2016

Menetelmän kehitys tapahtui osana tutkimusta Tampereen Teknillisessä Yliopistossa. Kyseisen menetelmän vaatimuksina oli että sillä pystyttäisiin sekä kvantitoimaan että kvalifoimaan metanolia ja furfuraalia torrefaasitiivisteestä. Kyseinen tiiviste on torrefaasin sivutuotteena syntyvä neste, jolla ei ole juurikaan arvoa energiantuotannon kannalta tai muuta arvoa. Tutkimuksen tarkoituksena oli selvittää, voiko kyseistä tiivistettä käyttää ravintona mikroleville ja näin edistää niiden kasvua. Tämä tiiviste sisältää metanolia ja furfuraalia, jotka ovat mikrolevien kasvua edistäviä yhdisteitä. Kyseinen tiiviste on kuitenkin hyvin hapanta ja siksi se täytyy esikäsitellä ennen käyttöä. Tutkittavien esikäsittelymenetelmien toimivuuden tarkistamiseksi tarvittiin menetelmä, jolla voitaisiin määrittää kuinka hyvin esikäsittely poistaa happoja vaikuttamatta furfuraalin ja metanolin pitoisuuksiin.

Menetelmä kehitettiin kaasukromatografimassaspektrometrille, jossa oli headspace – näyteotin. Kyseisellä laitteella pystytään samanaikaisesti sekä tunnistamaan aineita että määrittämään niiden pitoisuuksia. Pääsasiallisesti menetelmän kehityksessä keskityttiin laitteen asetuksiin, kuten lämpötilaohjelmaan. Näytteiden käsittely ja valmistus ei ollut niin tärkeä tekijä, koska menetelmässä käytetyn headspace-annostelijan toimintatavan vuoksi näytteisiin ei tarvitse yleensä lisätä mitään: Ongelmia aiheutti pääasiassa se ettei näytteitä laimennettu riittävästi. Näytteiden käsittely keskittyi siihen, että näytteitä laimennettiin riittävästi saturoinnin estämiseksi. Menetelmän ohjelma optimoitiin niin että näytteiden kromatogrammien piikit erottuivat toisistaan eivätkä asettuneet päällekkäin. Samalla kuitenkin menetelmä ei ole liian pitkä ajallisesti. Ohjelmoinnin lisäksi menetelmää yritettiin säätää niin, että sillä voitaisiin analysoida myös etikkahappoa, koska sen pitoisuus tiivisteessä on suuri ja sen pitoisuuden muutoksia haluttiin seurata. Myös näytteiden suolaamista ja headspace-injektorin asetuksia tutkittiin yhdisteiden haihtuvuuden parantamiseksi.

Menetelmälle oleelliset parametrit tarkistettiin ja optimoitiin niin että tuloksena oli menetelmä, jolla pystytään tarkasti määrittämään metanolia ja furfuraalia. Suolaustestien vuoksi menetelmällä on myös vaihtoehtoja joitten avulla tuloksia voidaan halutessa parantaa.

Avainsanat: Headspace, torrefaasi, bioenergia, pyrolyysi

CONTENTS

INTRODUCTION

This thesis is an assignment submitted to Tampere University of Technology as a part of one of their studies into renewable sources of energy. The goal of the assignment was to develop a method with which to analyze torrefaction condensates and how different pretreatments changed the compound concentrations. The method was developed for GC-MS.

The torrefaction condensate was from a torrefaction process where timber was dried to lower their weight to make transportation more efficient. The condensate contains various acids, organic molecules, water and other compounds and unlike the torrefied biomass itself it has no energy value. However, it is possible to use it to enhance other biofuel production cycles. In this case the product was being studied to make it suitable for use as a growth feed for microalgae.

Torrefaction produces different compounds that are good for microalgae, but also others that inhibit their growth or are poisonous to them. In this case the compounds of interest were methanol, furfural and acetic acid. Methanol and furfural are beneficial to microalgae and acetic acid is poisonous. The goal of the study was to find a treatment which would lower the acetic acid concentration without affecting the concentrations of methanol and furfural too much. To determine the effectiveness of the pretreatments, a method was required that could accurately measure the concentrations of the different compounds that one was interested in.

The method was optimized for the quantitative analysis of methanol and furfural with experiments been done on making it work with acetic acid as well. In addition to this experiments were conducted on optimizing sample preparation as the method relies greatly on how well the volatile compounds in the samples can be evaporated.

1 THEORY

The method development was done as a part of a research project on how to improve several different processes with which one can turn biomass into different organic fuels. The processes that this project studies are pyrolysis and primarily torrefaction.

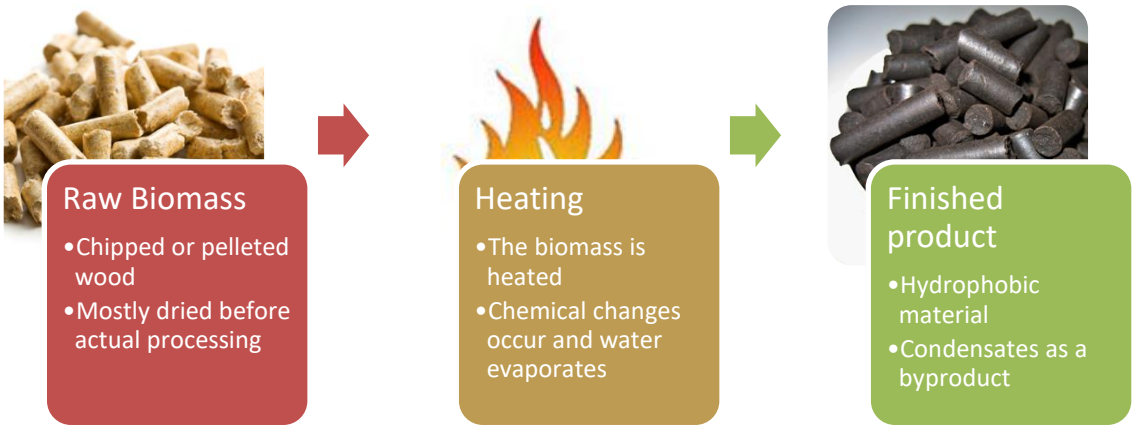
1.1 Pyrolysis

Pyrolysis is a thermal decomposition process where biomass containing long strands of hydrocarbons like cellulose, hemicellulose and lignin, when exposed to high temperatures (300-500 ºC) in oxygen less environment break down into other less complex compounds (Picture 1). Pyrolysis is one of the most important chemical processes used in the industry as in addition to fuels the process is used in the production of charcoal, activated carbon and chemicals for production of plastics. Pyrolysis is in short a very versatile chemical process and has numerous uses and applications. It should not be however confused with torrefaction which happens at 200 to 300 ºC (JR Jones 2011).

In the last decade or so, pyrolysis has garnered more interest as a means of producing fuels. The interest is understandable, as not only can the process be used to make fuel from renewable sources such as wood, but it can be used to process waste material as well. Considering the amount of waste produced each year globally, it is easy to see why pyrolysis is such an attractive solution to worlds energy problems (Assoc. Prof. Basak Burc 2005).

1.2 Torrefaction

Torrefaction is a thermochemical process where biomass is heated at 200-300 °C without oxygen. In this process water as well as other superfluous volatiles are evaporated out of the material and various biopolymers (cellulose, hemicellulose and lignin) partially decompose releasing other volatiles. The resultant product is a blackened, dry and solid material, which is often referred to as bio-coal, although it shouldn’t be mistaken for charcoal which is produced through pyrolysis (http://newenergyandfuel.com.torrefaction-a-new-process-in-biomass-and-biofuels).



Picture 1. Rough diagram of torrefaction (Source: http://torrefactie.nl/en/, modified)

The process through which bio-coal or other torrefied products are produced is often referred to as minor pyrolysis due to the fact both processes function on the same principles. Pyrolysis is one of the oldest chemical processes that mankind has used extensively; it is the same process through which tar is produced. The key difference with these two processes is that torrefaction happens at much lower temperatures and is currently mainly used to improve the handling of the biomass by reducing its weight by removing water and making it easier to grind for future processing. It also gives the biomass hydrophobic properties making storage easier and cheaper (Bergman. & Kiel. 2005).

The main advantage of torrefaction is that it is a relatively simple way of producing renewable energy. Most of the biomass used in torrefaction is wood and as such as torrefied products are burned, the carbon dioxide produced is absorbed by new trees being grown and is as such a carbon free method of producing energy. This makes torrefied products a very good source of fuel in countries with access to large quantities of torrefiable biomass, such as wood (Johnson. 2007. Torrefaction - A Warmer Solution to a Colder Climate).

1.3 Premise

The method development was done as a project with focus on the condensable gasses and other liquids that are released in the process. Around 50% of raw wooden biomass's weight is water, which is a limiting factor for the energy value of the product, and in addition to water there are other compounds in wood that are produced or released through the heating process. This condensate has no significant value in energy production as it in general doesn't contain compounds that are suitable for energy production. This forces producers of torrefied biomass to find some means to either dispose or store this condensate which increases the costs of the production. This factor makes torrefied biomass less viable as an economic alternative to traditional energy sources such as oil. In addition, the condensate is highly acidic, another factor which makes it unviable as a fuel: the acidic properties would cause corrosion in any engines it was used.

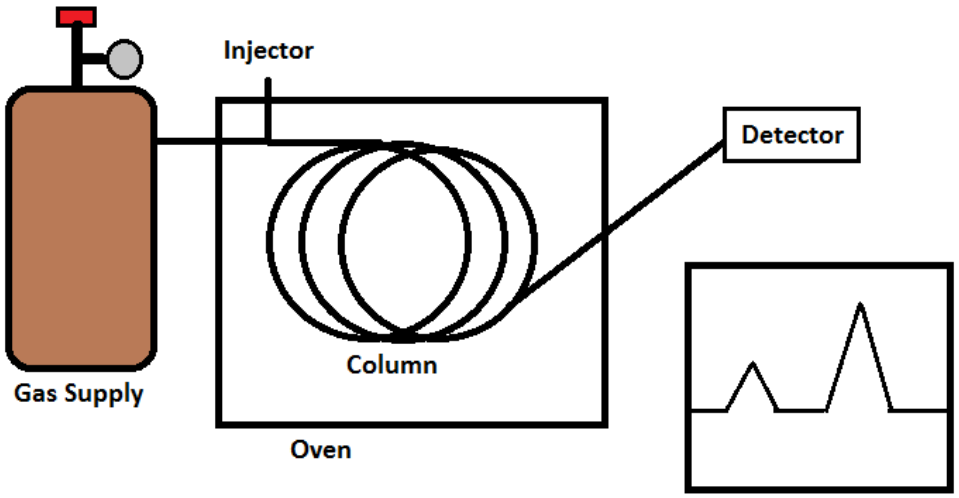
The condensate however could be as feed for biomass growth. The liquid in question contains aldehydes, methanol and other compounds that various microalgae use in their metabolic reactions and their addition into the growth medium could increase their production rate. This is a very important point to consider since microalgae and biofuels made from them are one of the most important sources of renewable energy currently being studied. By using the condensate from torrefaction the overall efficiency and productivity of both processes could be increased. The use of the condensate however is not without its problems: namely that torrefaction produces harmful compounds as well. Torrefaction also produces acids, mainly acetic acid, that are toxic to microalgae or are otherwise harmful to them. It cannot be therefore used in its intended purpose without some form of pretreatment.

These pretreatments were the focus on the study of using the torrefaction condensate for growing microalgae. The study was conducted in Tampere University of Technology, facility of Biotechnology. As there were numerous compounds that had to be studied in the condensate, an analysis method was required that could be used to quantify and detect these compounds simultaneously. Standard gas chromatography would have been suitable as it could be used to quantify different chemicals. The problem with regular gas chromatography would have been that it would require standards to which compare the retention times of different compounds in the samples themselves to identify them.

This would have been time consuming and one wouldn't have been able to identify different compounds without first having to identify them using some other method. As such using a GC-MS was considered optimal for this as it can qualify and quantify chemical compounds simultaneously

1.4 Chromatography

The principle behind Gas Chromatograph Mass Spectrometry (GC-MS) and by extension Gas Chromatography (GC), is that various compounds have different temperatures at which they evaporate. By injecting the sample into a column that runs through an oven the temperature in the column can be raised gradually so that different compounds are separated from another based on their evaporation temperatures. Once the compounds have evaporated, it is carried through the column by a gas flow that is composed of an inert gas such as helium. From the column the gas and the evaporated compounds flow into a Flame Ionizing Detector (FID) which through the use of intense heat ionizes the different compounds, which allows the detector to detect these compounds through changes in voltage running through it. The changes in the voltage are interpreted as peaks on a chromatogram and form the peaks area, when compared to peaks from standards, the compounds quantity can be calculated. (Pavia, Donald L., Lampman, Kritz, Engel. 2006)



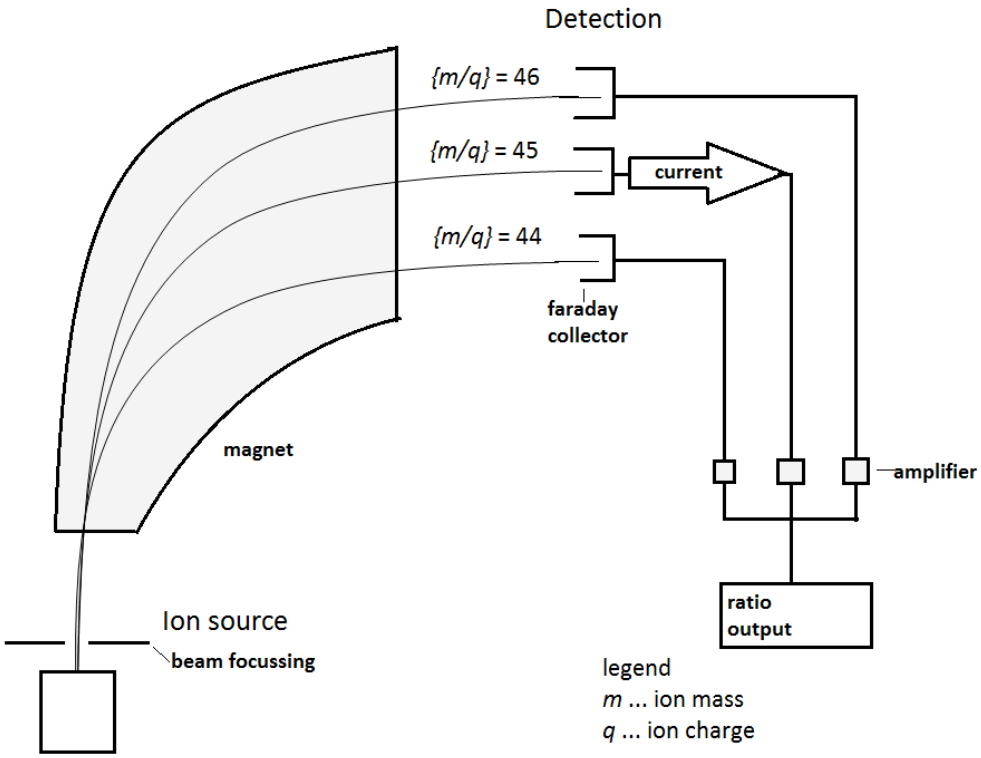
Picture 2. A GC-MS analysis tool and its main components (Source: birgin-ham.ac.uk, modified).

1.5 Mass Spectrometry

Mass spectrometry is an analysis method where different compounds are identified based on their atomic mass. In a mass spectrometer, the sample is accelerated and bombarded with electrons so that the molecules become ionized. These ionized particles are then accelerated through a magnetic or electrical field, which causes the particles to separate from another based on their mass to charge ratio. Other factors contribute to the separation such as Newton's second law due to the different masses of the ions. (Picture 3)

The ions are detected with a series of faraday collectors which are hit with the ions and these cause changes in current flowing through the collectors, which is detected by the spectrometers software. The ions mass is determined by which of the detectors the ions hit, as in a constant magnetic field different ions have predictable trajectories and therefore the collectors are placed in such a way that the ions hit specific collectors (Hoffman & Stroobant. 2007).

The number of different ions is determined by relative abundance as the amounts of different ions vary based on the analyzed compounds composition. The relative abundance of different ions is then used to determine what the compound is as the ratio of different ionized elements remains the same as in a chemical formula (Vilpunaho. 2014).

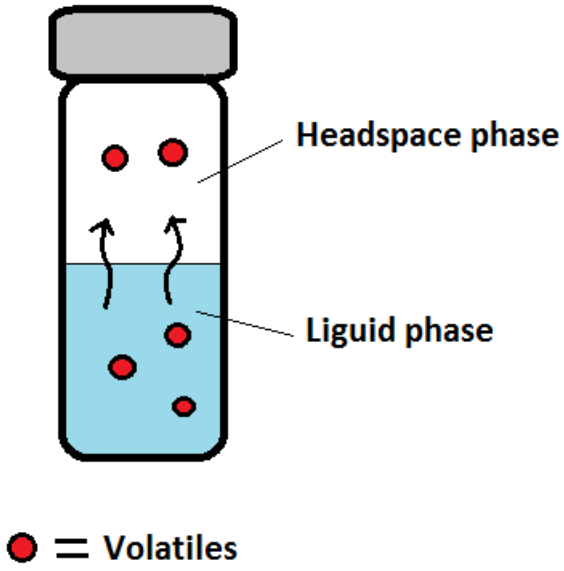


Picture 3: A faraday collector and its components (Source: gwadi.org, modified).

1.6 Headspace Sampler

A headspace sampler is a tool which can be linked to a GC or GC-MS in the place of an ordinary sampler. In most standard samplers, the sampler uses a needle to inject a volume of liquid sample into the injection port where heat evaporates the sample and allowing it to elute through the column.

In headspace sampling however no liquid is injected. Instead the sample is put into a headspace oven which heats up the sample releasing volatile compounds within the sample. When a sample is taken, the sample is a volume of the gas above the liquid sample into which the volatile compounds have evaporated into.
The gas is directed through a transfer line into the injection port and from there into the column (Stenerson & Verma 2011).



Picture 4. An illustration of a headspace sample bottle and its working mechanism (Source: share.psu.ac.th, modified)

2 METHODOLOGY

In this section the tools, reagents and tests used in the method development are explained and listed.

2.1 Analysis tools and reagents

The primary analysis tool used in the method development was Agilent G1701EA GC/MSD ChemStation.

Picture 5. The GC-MS. Note the loop connecting the tool to the headspace sampler.

The GCMS and headspace sampler work by collecting a sample of gasified volatiles from a 20-ml sample bottle. This sample is then channeled into the GC-MS through an insulated loop.

Picture 6. The headspace sampler.

The chemicals and compounds used for sample and standard preparation were the following:

5% methanol (made by measuring 5 ml of 100 % methanol into a 100 ml bottle and then diluting it with Milli-Q water to a volume of 100 ml)
5% acetic acid (made from 100 % acetic acid same way as methanol)
1% furfural (the furfural solution was made earlier by someone else)
Milli-Q water
Sodium Sulfate (NaS)
The samples that were used for comparison and resolution test with the temperature referring to the temperature in which they were pretreated:

Torrefaction condensate (pretreated by heating at 300 °C)
Torrefaction condensate (pretreated by heating at 275 °C)
Torrefaction condensate (pretreated by heating at 225 °C)

The total volume of samples and standards was fixed at 240 µl to keep the headspace volume constant. The volume was chosen because there wasn't a particularly large amount of the condensate available and it was needed for both the method development and retreatment tests.

2.2 First batch of experiments

The first batch of experiments was done with an already existing method to see if it could be used as a basis for our method. This method was originally developed for the analysis of methanol using headspace-sampling, but not for the analysis of torrefaction products.

2.2.1 Temperature program 1, 2 and 3

The first experiment as stated before was a pre-existing method and is referred to as program 1 in the results. It used the following parameters:

Inlet heater: 250 °C Pressure: 13.3 psi
Total Flow He: 12.3 mL/min
Oven temperature program
40°C (4 min), 8 °C/min to 60 °C, 5 °C/min to 85 °C (2 min), 30 °C/min to 220 °C (2 min)
Headspace:
Oven: 80 °C Loop: 100 °C Transfer line: 120 °C
Vial equilibration: 2 min Vial pressurization: 0.1 min
Loop Fill: 0.5 min Loop Equilibration: 0.1 min

The standards for the test were prepared by pipetting calculaed amounts of stock solutions and milli-Q water into 20 ml sample bottles. The bottles were then sealed with airtight rubber-aluminum caps. (Table.1)

Table 1: First standard concentrations and the volumes of reagents used

Methanol

Concentra-tion (g/L)	Stock V (µl)	H_2O V (µl)
0,5	24	216
1,0	48	192
1,5	72	168
2,0	96	144
2,5	120	120

Furfural

Concentra-tion (g/L)	Stock V (µl)	H_2O V (µl)
0,1	24	216
0,2	48	192
0,3	72	168
0,4	96	144
0,5	120	120

2.3 Second batch of experiments

The second stage of oven temperature programming was started with programming the oven temperature to the following:

35°C (hold 1 min)
10 °C/min to 250 °C
250 °C (hold 4min)

This was done to check the resolution of the method at this stage and when methanol and furfural elute through the column. This was program 2.

The first test was to simply run a sample 300°C condensate diluted to half of its original concentration with the method and check the retention times and resolution and adjust the ramp accordingly.

After the first test the temperature program was adjusted for a slower ramp to improve the resolution and the resolution was tested again.

35°C (hold 1 min)
5 °C/min to 250 °C
250 °C (hold 4min)

After the second test the program was again adjusted, but this time so that the temperature rose faster after furfural had eluted through the column to cut down run time to a more manageable length. This was program 3.

35°C (hold 1 min),
5 °C/min to 155 °C,
10 °C/min to 250 °C
250 ° (hold 4min)

2.4 Sample repeatability

At this stage the oven temperature program had been worked on for a while and it was prudent to check if the inaccuracy of the results was due saturation or did the temperature program require further improvement. As such the method's repeatability was tested to see how much variance there was between the results. This was done with eight samples of torrefaction condensate (300 °C) diluted to 1/4 of their original concentration.

2.5 Final standard concentrations

After the repeatability test the standard concentrations were adjusted to their final concentration and then tested.

Methanol: 0.1; 0.2; 0.3; 0.4; 0.5 and 0.6 g/L
Furfural: 0.05; 0.10; 0.15; 0.20; 0.25 and 0.30 g/L

The last standards (0.6 and 0.30 g/l) were chosen to continue the standard curve to see if it was still linear at those concentrations. These were prepared by pipetting the amounts indicated (table 2) into 20 ml sample bottles.

Table 2. Final standard concentrations and the reagents used

Standard (g/L)	Methanol V µL	Furfural V µL	H_2O µL
0,1/0,05	4,8	12	223,2
0,2/0,10	9,6	24	206,4
0,3/0,15	14,4	36	189,6
0,4/0,20	19,2	48	172,8
0,5/0,25	24,0	60	156,0
0,6/0,30	28,8	72	139,2

2.6 Salting and headspace experiments

Near the end of the method development, one point of interest with the method, was to see if salting the samples could be used to improve the evaporation of different volatile compounds within the samples. This was done by adding sodium sulfate into the samples.

Additionally, the use of lower headspace oven temperature was tested with and without the salting. This was done to see if salting could be used to overcome the effect of lower headspace oven temperature.

For this test the samples that were chosen were 0.5 g/L methanol, 0.2 g/L furfural and a sample of the condensate (300 °C) diluted to a fourth of its original concentration. Four of each sample were prepared, two to be salted and another two to not be.
One salted and one unsalted sample was run with the headspace oven at 80 °C and the other two were run at the temperature of 60 °C. The amount of sodium sulfate used per sample was 17 mg.

After the first test the salting was tested with three different condensates to see how this effected their results. The amount of salt that was used in this was the same as in the first test.

Samples
- Torrefaction condensate heated at 300 °C
- Torrefaction condensate heated at 275 °C
- Torrefaction condensate heated at 225 °C

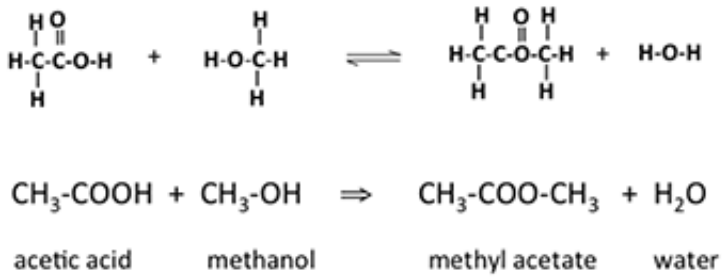
2.7 Acetic acid tests

Between the previous tests numerous tests were run with acetic acid to quantify it. The first test was a 0.25 g/L acetic acid sample run without solvent delay (1 min) to see if this affected the results. The second test was run with a similar sample, but this time with the headspace oven temperature lowered to 60 °C. Final test was to see if methanol and acetic acid reacted with one another to create methyl acetate, which was present in the condensate in large amounts: Most likely the result of acetic acid reacting with methanol.

2.7.1 Methyl acetate test

As the concentrations of methyl acetate were higher than those of acetic acid, this test was done to see if methyl acetate could be made to react with methanol and the produced methyl acetate used to indirectly quantify acetic acid.

Samples were prepared with different concentrations of acetic acid and methanol mixed together to see if the two compounds reacted with each other. The samples were prepared from 1 % acetic acid solution and 1 % methanol solution by pipetting indicated volumes of acetic acid, methanol and milli-Q water into 20 ml sample bottles. (Table 3)



Picture 3. The reaction of acetic acid with methanol

The reaction that this test relied on is one form of esterification and happens in highly acidic conditions. The condensate itself is very acidic (although the reaction usually requires sulfuric acid, a strong acid, specifically to occur) and the reaction occurs at high temperatures so it is possible that the reaction did occur in the initial production of the condensate (Mallaiah & Venkat. 2015).

Table 3. Pipetted volumes for the standards

Acetic Acid V (µl)	Methanol V (µl)	Water V (µl)
0	120	120
24	96	120
48	72	120
72	48	120
96	24	120
120	0	120

Table 4. Methyl acetate test standard concentrations (see pipetting chart for the volumes)

Sample	Acetic acid (g/L)	Methanol (g/L)
1	0	0,5
2	0,1	0,4
3	0,2	0,3
4	0,3	0,2
5	0,4	0,1
6	0,5	0

3 RESULTS

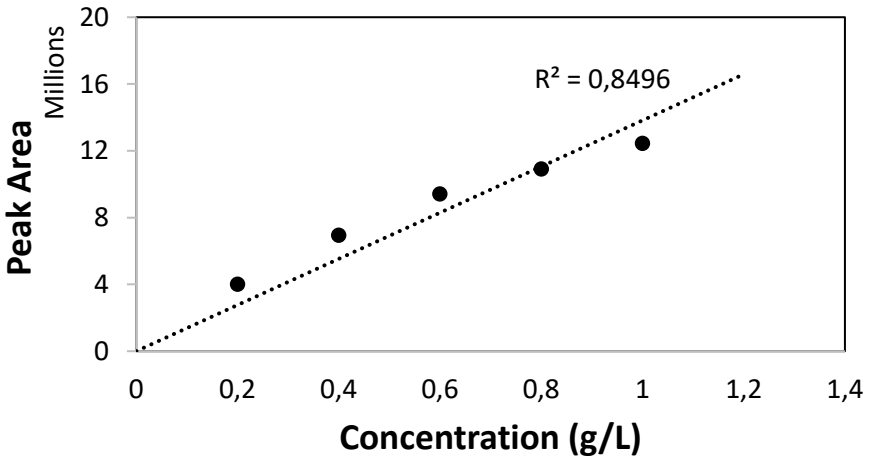
In the following chapter the various results are displayed under the same names as they are called in the methodology.

3.1 First batch results

The first batch of tests were done with the purpose of seeing if an already existing method could be repurposed for the needs of the project. This did not happen as the accuracy and correlation were not good enough for the intended purpose.

As can be seen from the standard curves, the correlation of the results wasn't high enough to produce accurate results. The inaccuracy of the results is most likely due to two different factors: oven temperature rising too quickly and sample saturation. The first problem resulted from the fact the GC-MS couldn't create accurate peaks due to too much of the sample eluting through the column too quickly. The second problem is due to the fact the air in the headspace sample bottles can only absorb limited amounts of evaporated compounds before becoming saturated. (Figure 1)

(a) Methanol



(b) Furfural

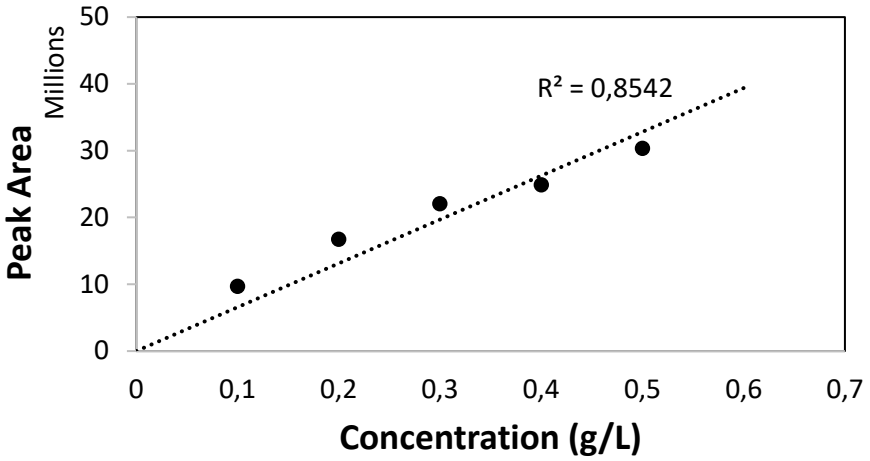


Figure 1. Standard curves for (a) methanol and (b) furfural with GC-MS-HS program 1

The chromatogram shows that while furfural and methanol peaks are visible, the method is too short for the compounds to properly separate in the column (furfural peak is overlapping with another peak). The sample was the condensate pretreated at 300 ºC. (Figure 2)

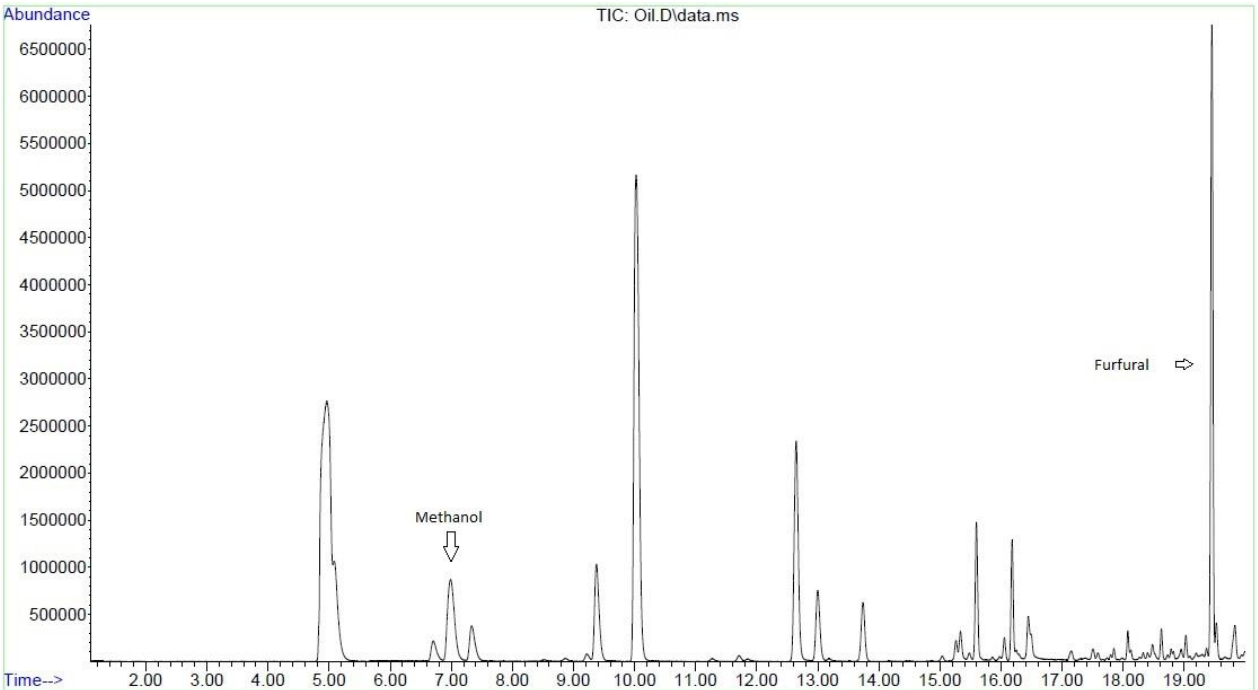


Figure 2. Chromatogram of torrefaction condensate with program 1

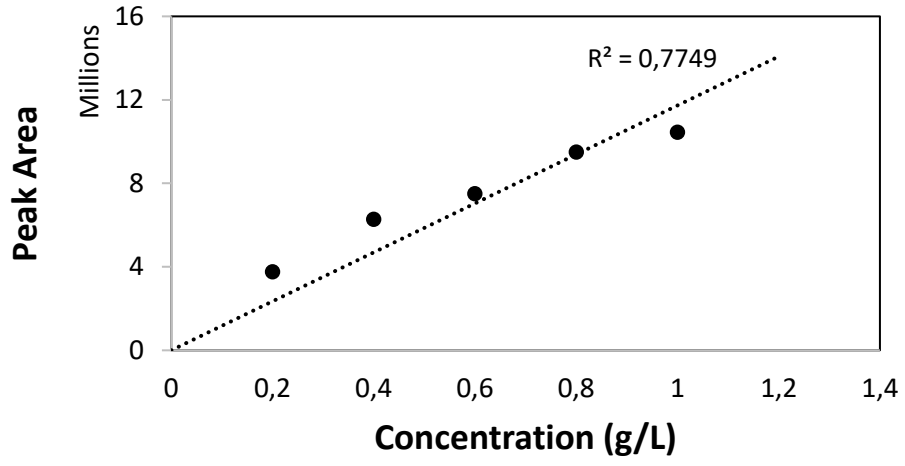
3.2 Second batch test results

In this part of the method development the results that were looked were primarily whether different compounds could be identified and how separated they were from each other in the chromatogram.

3.2.1 Program 2 results

In the second experiment the temperature program was adjusted so that the temperature rose linearly and was considered an intermediate program that would be refined based on how accurate the results are and the elution temperatures of the compounds. Based on the standard curves and chromatogram the temperature rose too rapidly resulting in inaccurate results.

(a) Methanol



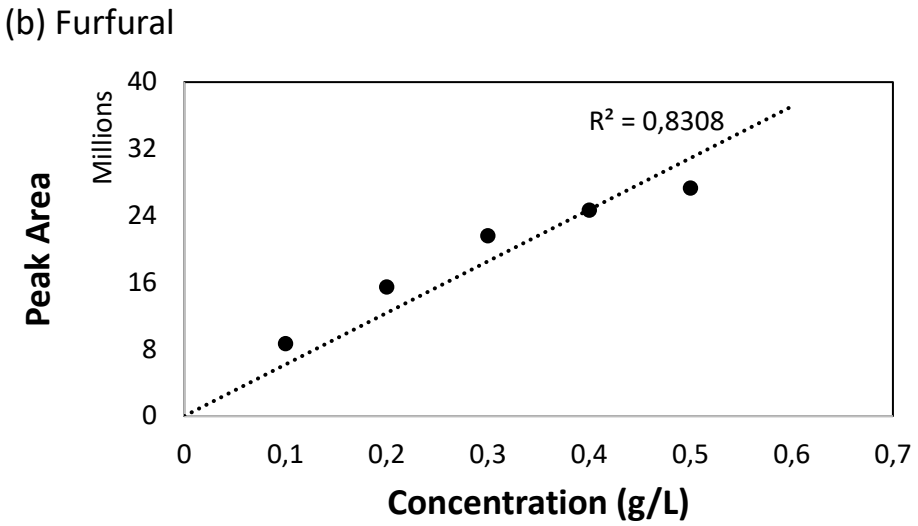


Figure 3. Standard curves for (a) methanol and (b) furfural with GC-MS-HS program 2

As can be seen from the chromatogram, the peaks for methanol and furfural are clearly visible. However, at this point there is still overlapping with other peaks which meant that the methods temperature gradient should be lowered. The sample used was the condensate pretreated at 300 ºC. (Figure 4)

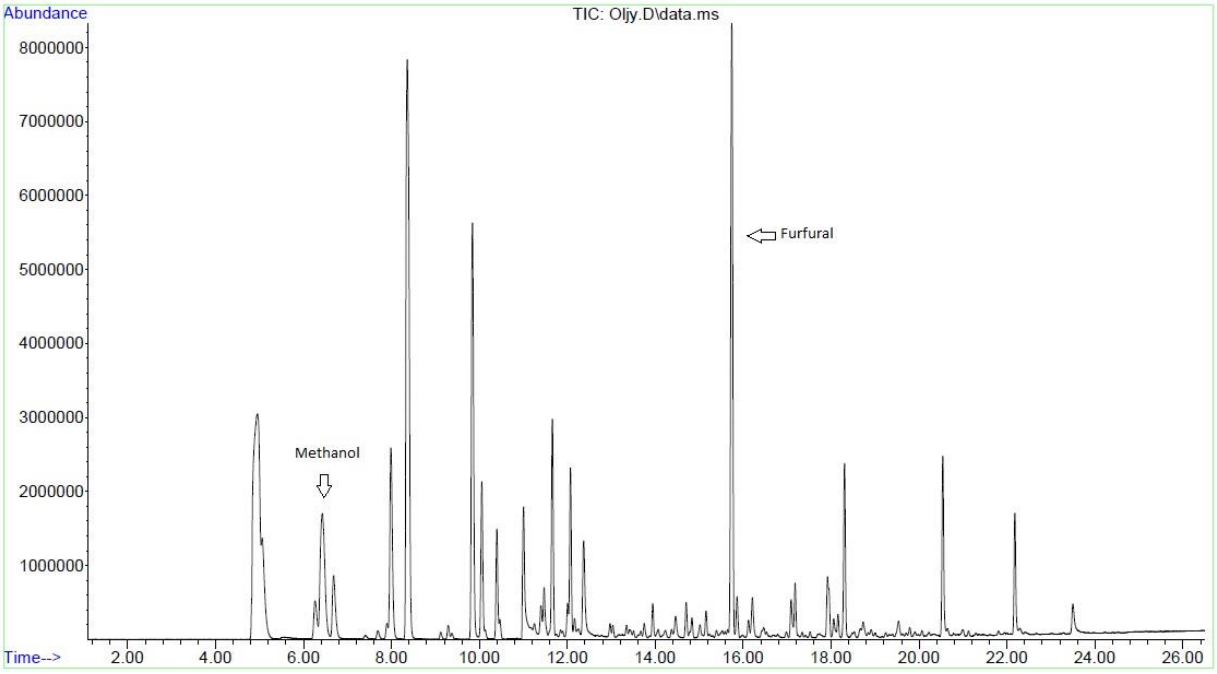


Figure 4. Chromatogram of torrefaction condensate with program 2

3.2.2 Second resolution test

The decrease in the temperature gradient resulted in a better resolution (figure 5) and based on the result the next course of action was to shorten the run time, by increasing the gradient after 24 minutes. The oven temperature program was changed so that after 24 minutes the temperature would rise 10 °C/min decreasing the run time from 48 minutes to 38 minutes and standard concentrations were lowered to account for saturation.

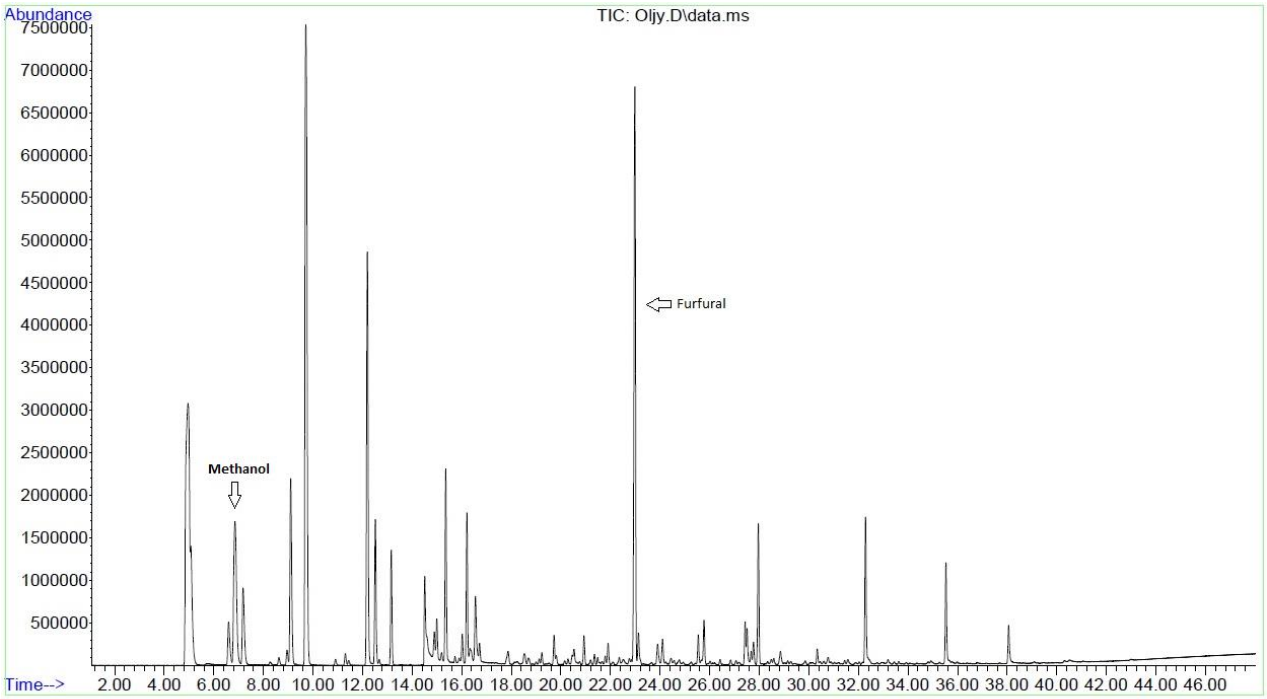


Figure 5. Chromatogram of torrefaction condensate with intermediate program

3.2.3 Repeatability

By testing the variance between the samples of pretreated condensate, we were able to confirm that there is minor variance between different tests with the same sample (2-3 %) and as such the previous inaccuracy was more likely caused by saturation of the samples. Based on this conclusion during the last phase of the testing, the standards' dilution was increased to prevent the headspace from becoming saturated. The samples were diluted to one fourth of their original concentrations. (Table 4)

Table 4. Repeatability test results. The concentrations are shown with the dilution been accounted for.

Methanol	Peak A	g/L
Sample 1	7417698	1,484
Sample 2	8227266	1,645
Sample 3	7951912	1,590
Sample 4	7916127	1,583
Sample 5	7778098	1,556
Sample 6	8022923	1,605
Sample 7	7859104	1,572
Sample 8	8001468	1,600

Average	1,579
Standard deviation	0,047
STDV (%)	2,968

Furfural	Peak A	g/L
Sample 1	20293544	0,812
Sample 2	21467633	0,859
Sample 3	20445392	0,818
Sample 4	20273140	0,811
Sample 5	20189336	0,808
Sample 6	20579612	0,823
Sample 7	20105650	0,804
Sample 8	20025354	0,801

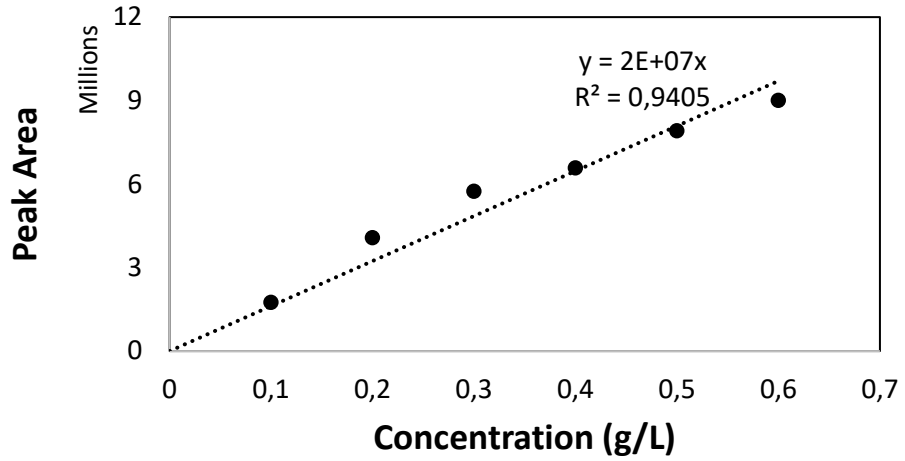
Average	0,817
Standard deviation	0,018
STDV (%)	2,243

The results are generally uniform throughout the sample series, but there is still some variation between them. Most likely due to the small amounts of sample that were pipetted, which can cause inaccuracies in the results. This is discussed in detail in conclusions and discussion.

3.2.4 Third resolution test

The third and final resolution test was done with standards. The temperature program raised the temperature slower than before and as such the results were more accurate (figure 6): accurate enough that the method was considered ready to use in the analysis of torrefaction condensates. There was also a good separation of compounds in the chromatogram. Program: 35°C (1 min), 5 °C/min to 155 °C, 10 °C/min to 250 °C (4min). (Figure 7)

a) Methanol



b) Furfural

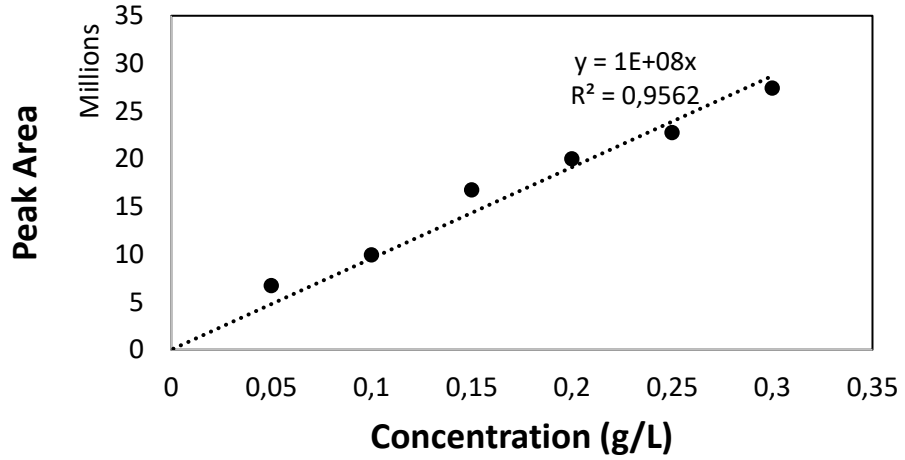


Figure 6. Standard curves for (a) methanol and (b) furfural with GC-MS-HS program 3

The separation of the compounds was tested by running a sample of condensate (pre-treated at 300 ºC) with the program 3 and checking the chromatogram. The resolution and the separation of the compounds was such that at this point the oven temperature program was considered optimized. After this the method was tested for repeatability and salting and headspace oven parameters were tested.

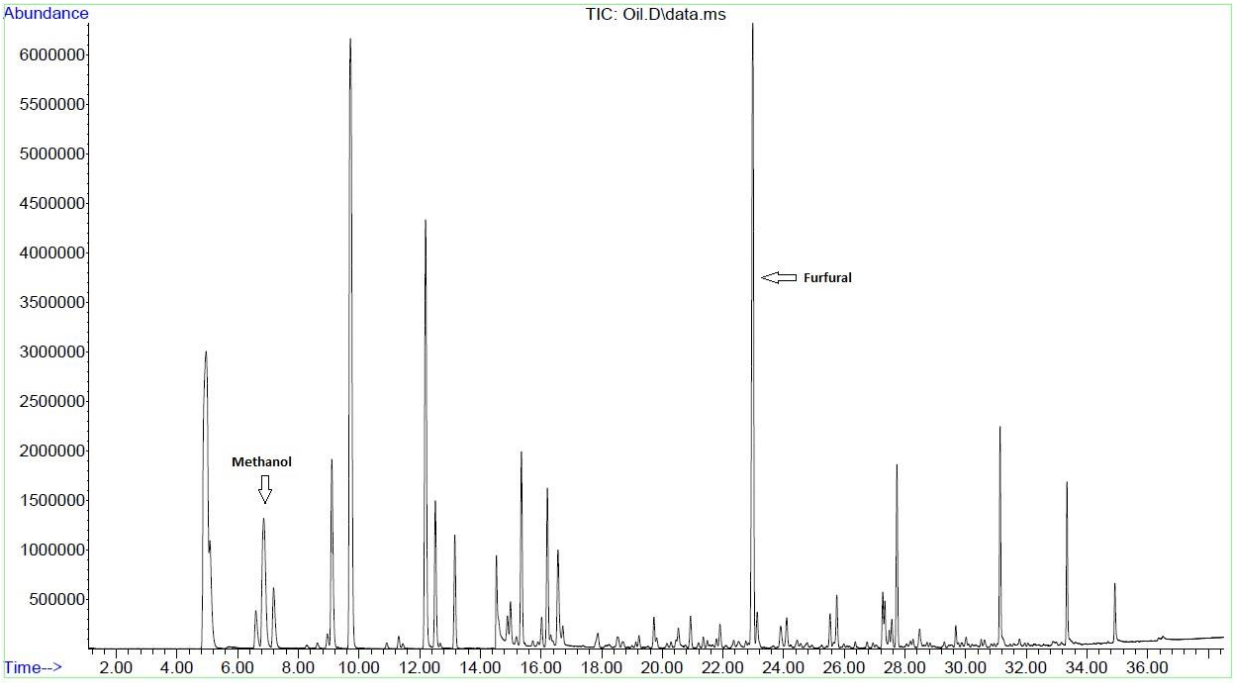


Figure 7. Chromatogram of torrefaction condensate with program 3

3.3 Salting tests results

Salting of the samples produced interesting results as in both of the experiments there was a clear increase in how much of the volatile compounds was evaporated. This means that salting can be potentially used to make results more accurate.

3.3.1 First salting test results

As can be seen from the chart salting increased the evaporation of volatile compounds in the samples by a large margin. The results also show that the results are much closer to what they should be with the salted samples. While previous experiments have shown that the method can be used to accurately quantify methanol and furfural, there appears to be some variance on how well volatile compounds evaporate between each of the sample sets.

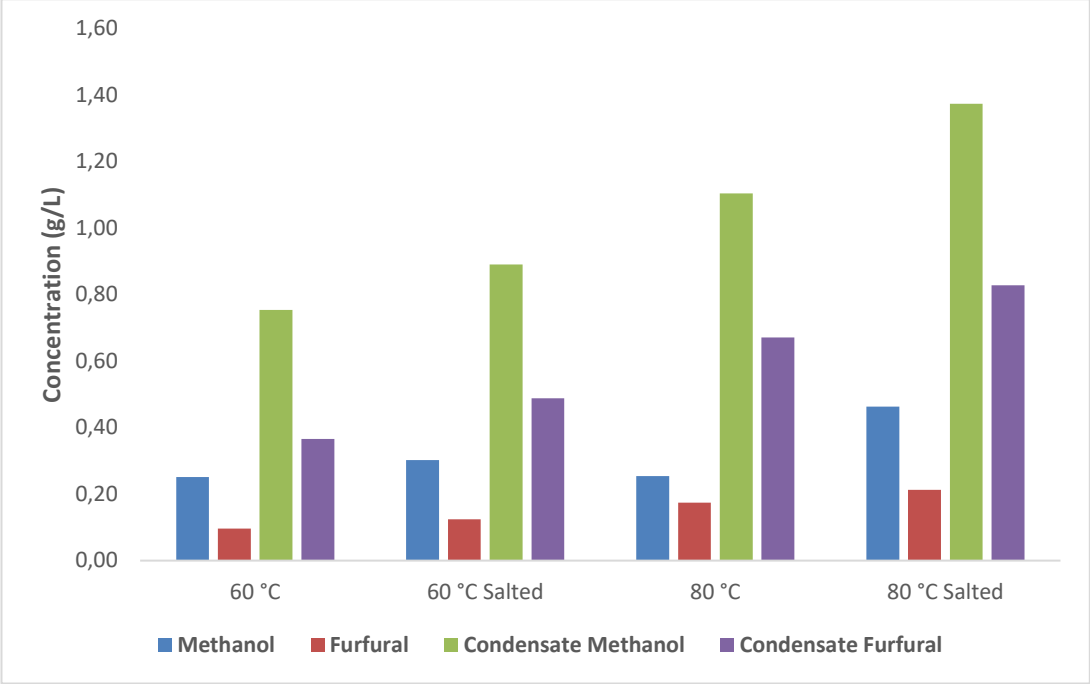


Figure 8a. Effect of HS oven temperature and salting on concentrations of methanol and furfural in the samples. Methanol and furfural standards represents 0.5 g/L and 0.2 g/L respectively. Torrefaction condensate (300 ºC) is considered the test sample. (a) Concentration graph of methanol and furfural; (b) chromatogram of torrefaction condensate

Additionally, the effects of salting can also be seen from the overlapping chromatograms. Salting increased the amount of methanol and furfural that was evaporated in the headspace sampler and as such the peaks were larger.

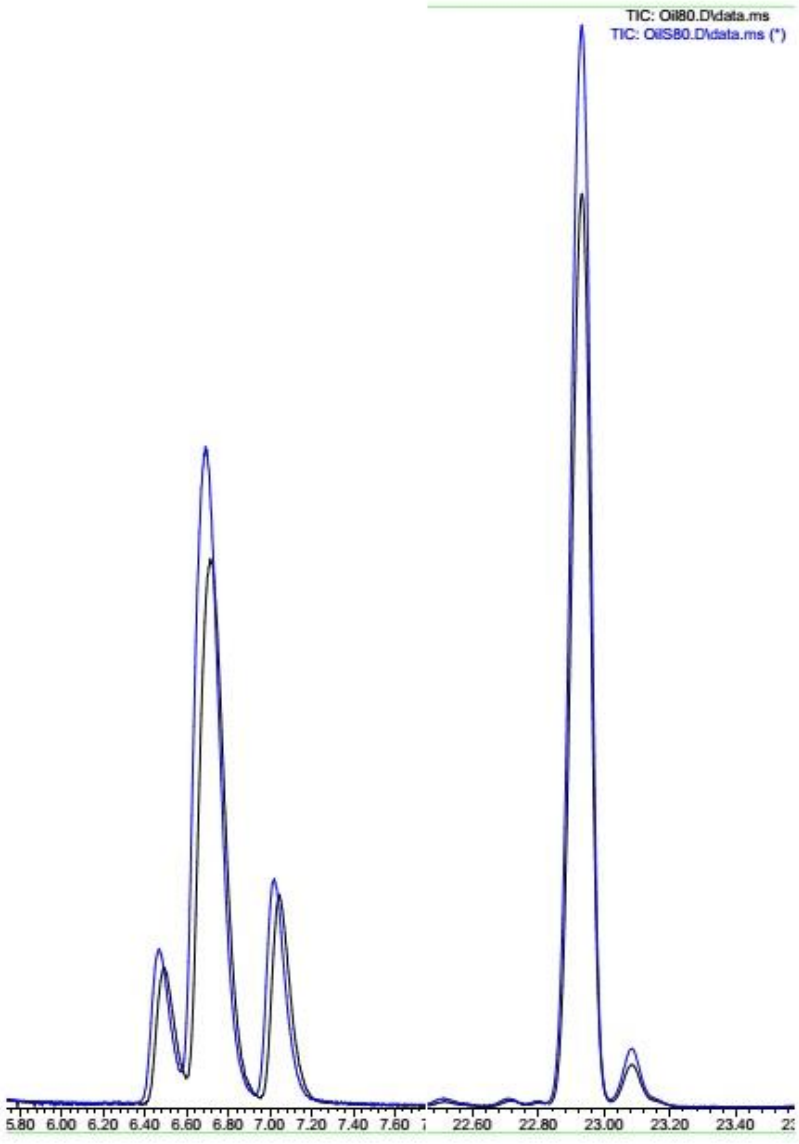


Figure 8b. Chromatogram overlay of results of methanol and furfural at different headspace temperatures.

3.3.2 Second salting test results

As with the first salting test, there was an increase in the evaporation of different volatile compounds thanks to salting. After this test it was confirmed that salting has its potential uses in conjunction with the method. The numbering stands for the temperatures at which the condensate samples were pretreated.

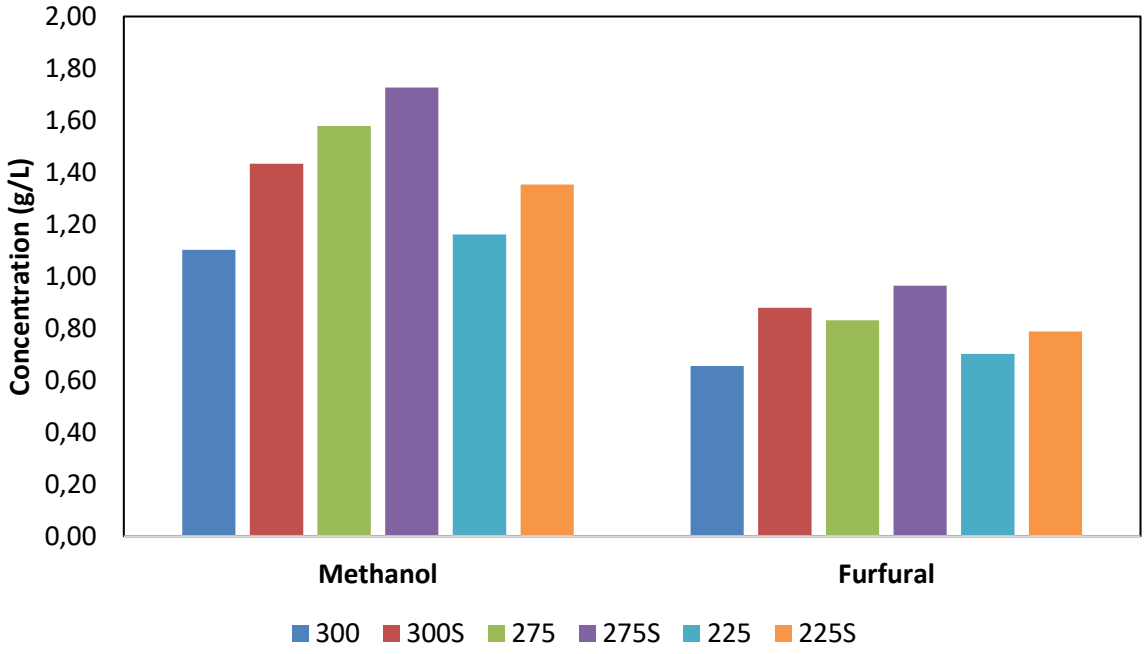


Figure 9. Effect of salting on the methanol and furfural concentrations in torrefaction condensates prepared at different temperatures with S standing for salted (the numbers indicating the pretreatment temperatures of the condensate samples in °C (300=300 °C and so on))

3.4 Acetic acid results

Acetic acid produced no results with peaks. This was most likely due to the column that was used and any alternative columns that were available were of the wrong type as well. Nevertheless, numerous attempts were made to measure acetic acid, but none of them worked.

In addition, methanol and acetic acid did not react with each other and no methyl acetate peaks were produced. For this reason, it was decided that tests with acetic acid should be stopped to conserve time.

4 CONCLUSIONS

The method reached a point in its development where it could be used for the quantitative analysis of methanol and furfural. And since numerous other compounds are shown on the chromatograms from the samples, the method could be in the future optimized for the analysis of other compounds as well. Unfortunately, at this stage there is no indication of if this method can be used in the analysis of acetic acid, even with changes in the column model and type.

One problem that the method development faced during this time was the relatively high concentrations of the stock solutions. In most of the experiments the samples were pipetted by taking the necessary volumes of prepared stock solutions. This however led to a situation where the amounts of pipetted solutions were so small that it might have been more logical to dilute the stock further so that bigger volumes could be measured. Also, the sample volumes could have been increased as well. The samples are water soluble so this can be done and the samples themselves were mostly water originally. The solubility of the different compounds is not the problem however as saturation is a far bigger issue.

The salting of the samples was originally intended as a way acetic acid could be made visible in the chromatograms. But as it never showed even in pure samples, it was obvious that the problem wasn't with the evaporation but with the column. It was tested nonetheless as it could improve the evaporation for methanol and furfural. And as the results were positive with an increase in evaporated amounts, salting can be concluded to be a viable way of improving the accuracy of the method. And as it only requires adding a bit of sodium sulfate, it can be done without complicating the process unnecessarily.

In conclusion, the finished method can be still improved by finding better ways to make the samples. Note that the conditions for the method have been optimized for 20 ml sample bottles with the total volume of samples and standards being 240 µl. The sample volume can potentially be increased to make sample preparation easier if the volume is adjusted for all standards and samples.

Table 5. The GC-MS parameters and standard concentrations:

Oven	Inlet heater: 250 °C
	Total Flow He: 12.3 mL/min
	Pressure: 13.3 psi
Oven temperature program	35°C (1 min), 5 °C/min to 155 °C, 10 °C/min to 250 °C (4min)
Headspace	Oven: 80 °C
	Loop: 100 °C
	Vial equilibration: 2 min
	Vial pressurization: 0.1 min
	Loop fill: 0.5 min
	Loop equilibration: 0.1 min
Standards	Methanol: 0.1; 0.2; 0.3; 0.4 and 0.5 g/L
	Furfural: 0.05; 0.10; 0.15; 0.20 and 0.25 g/L

5 DISCUSSION

Development of a method that can be used to analyse torrefaction condensates was quite problematic at times due to the fact something similar hadn't been done before. Torrefaction is used primarily for production of dried and easily grindable solid fuels that serve pretty much the same purpose as wood fuels. There also hasn't been a great interest in analysing the condensates themselves. Clear majority of the studies done related to torrefaction were on pyrolysis, which is done at much higher temperatures. Pyrolysis is something that fuel producers are generally more interested in as the process can be used to make liquid and gaseous fuels. This makes pyrolysis far more versatile and attractive for fuel production. What this meant for the method development is that theory regarding the process and what to watch out for was relatively limited.

A problem caused by the limited interest in torrefaction was that very few methods had been developed to analyse torrefaction products, which was especially true for the condensate. As such method had to be developed with a time-consuming step by step process by first running a sample of the condensate to determine the elution temperatures of the compounds. Once the initial sample has been run the program is changed based on the results one step at a time to get more accurate results. This process is where the method is adjusted by determining the elution conditions of different compounds and the method is then adjusted to more optimal conditions based on previous results. All this meant that within the developments timetable it could be only optimized for methanol and furfural.

The consequence of this was that there was little time to adjust the GC-MS so that it could be used for the analysis of acetic acid as well as methanol and furfural. This was a major point against the success of the of the method development as acetic acid was a compound of interest as well. But as stated previously in the results, the tests that were conducted with acetic acid produced no results; specifically, the chromatograms showed absolutely no peaks for acetic acid even when there was nothing but acid in a sample. Due to this the only conclusion that could be drawn from this was that the column used in the gas chromatograph wasn't letting the acid through. Due to time constraints, a suitable column couldn't be found and tests on acetic acid were stopped to focus on other tests.

In addition, there were some problems with the analysis tool itself, as the device that was being used wasn't used very often. As such whenever there was a problem with it, it took some time to solve this problem. Additionally, few people were available who knew the analysis tool's functions accurately. The biggest problem was with the fact that the helium needed to run the GC-MS ran out at one point and it took four days to replace the supply. Otherwise any of the problems could be solved relatively quickly even if it all added up to slight delays in schedule.

Within the time constraints of the method development the positive aspects of the method however became apparent. Since there was no complex sample preparation involved, the samples could be made very quickly and could also be redone if needed as none of the reagents used were expensive or unavailable. Numerous samples could be run one after another without having to start the run again with each sample. Of course due to the length of the program used it could be a while before all the runs were finished.

One of the problems that the method still has are the saturation and sample sizes. The sample sizes are something that cannot be helped as this is the sample size that was one of the requirements for the method. The stock solutions should however be more diluted so that the pipetted concentrations wouldn't be so small as it causes inaccuracy to occur in the analysis. Another point to this is to possibly increase the volume of the samples if possible. How much the volume can be changed depends on how much of the condensate can be used in the experiments for which the method was developed. But the fact remains, that the sample volumes may have too small to accurately measure. The condensates were also oily so in small volumes some of it always was left in the pipet.

The method is not very complex nor was its development, but it is however what was requested and it was done on time. The project on the use of torrefaction condensate as a feed for microalgae, now has a method that can be used to quantify methanol and furfural in torrefaction condensate. The inaccuracy of 2-3 % was considered by the project supervisor to be acceptable. This inaccuracy is no problem in the analysis as the method was created to determine how much the different condensate pre-treatments affect the amount of methanol and furfural in the condensate.

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APPENDICES

Appendix 1. Standard curve 1 raw data

Table 1. The peak areas for the standards

Methanol

Conc (g/L)	Peak area	Rt (Min)
0,2	4006827	6,990
0,4	6948073	6,990
0,6	9404133	7,000
0,8	10915854	7,000
1	12448007	7,013

Furfural

Conc (g/L)	Peak area	Rt (min)
0,1	9713541	19,453
0,2	16749234	19,457
0,3	22063702	19,463
0,4	24922105	19,466
0,5	30378216	19,47

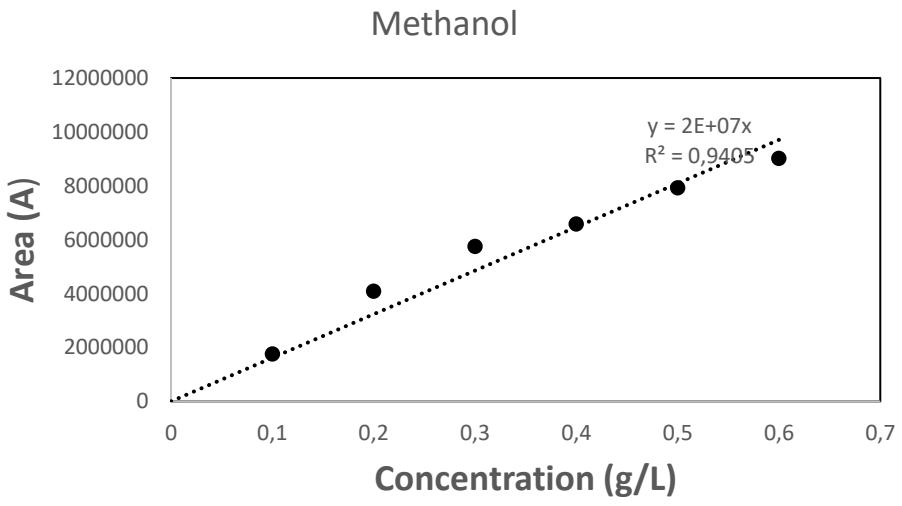
The peak areas are the integrated results for the peaks from the chromatograms.

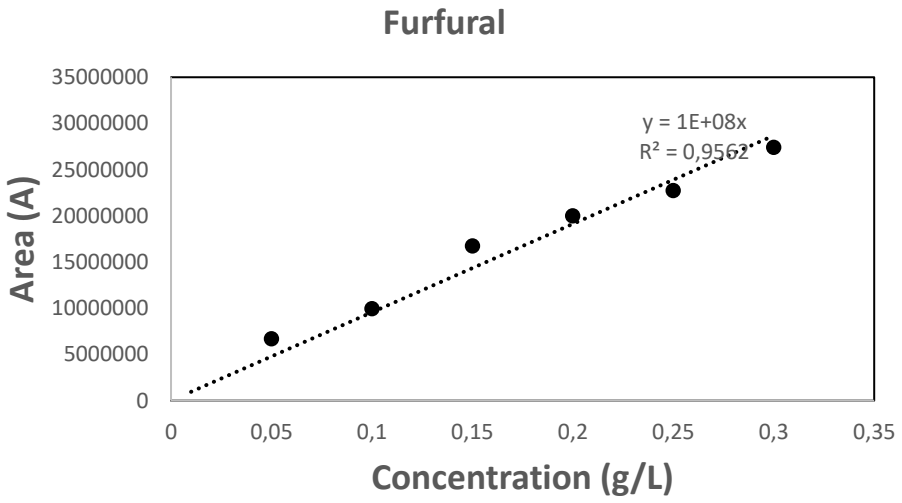
Appendix 2. Salting test 1 raw data

Table 1. The areas of the peaks for the different samples

	60 °C	60 °C Salted	80 °C	80 °C Salted
Methanol	5027505	6044369	5091716	9261707
Furfural	9661251	12422942	17392220	21295178
Condensate Methanol	3770780	4453634	5523575	6871123
Condensate Furfural	9155028	12200645	16768573	20703630

From the data the concentrations of the solutions were calculated by comparing the results to the standard curves:





The results for the condensates had to multiplied by 4 as the condensate samples had been diluted to ¼ of their original concentration