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Muconic Acid Process Development

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Nylon on tärkeä muovi, jolla on monia käyttötarkoituksia monilla teollisuudenaloilla. Sitä pääasiassa valmistetaan petrokemikaalijohdannaisista. Vaikka petrokemikaalivapaita reittejä on olemassa, ne ovat vielä lapsenkengissään ja niissä on ongelmia, joiden vuoksi ne eivät ole yhtä haluttuja kuin petrokemikaalireitit. Tämä insinöörityö tehtiin Teknologian tutkimuskeskus VTT:lle Tekesin rahoittamaa projektia varten.

Työn tarkoituksena oli kehittää biopohjaisen nylonin valmistamiseen käytettävän johdannaisen prosessia. Projekti aloitettiin tekemällä panosreaktoreilla kokeita, joilla selvitettiin, ovatko reaktorit vaikuttaneet tätä työtä edeltäviin VTT:n kokeisiin. Prosessin kehitysosuus aloitettiin tekemällä kokeita jatkuvatoimisella reaktorilla ja käyttäen hyödyksi panosreaktoreista saatua tietoa. Reaktiotuotteet analysoitiin käyttämällä GC-FID-menetelmää, mutta myös GC-MS- ja NMR-menetelmiä hyödynnettiin tässä työssä.

Panosreaktorikokeet osoittivat, että suurin osa panosreaktoreista oli vaikuttanut edellisiin kokeisiin. Toimivilla reaktoreilla tulisi tehdä vielä lisätutkimuksia, että reaktioiden toistettavuus voidaan varmistaa. Kokeet jatkuvatoimisella reaktorilla tuottivat hyviä tuloksia ja antoivat hyvää tietoa prosessista, huolimatta siitä että viimeisessä neljässä kokeessa oli ongelmia raaka-aineen kanssa. Jatkuvan reaktorin kanssa tulisi vielä tehdä jatkotutkimuksia ennen prosessin skaalaamista. Prosessi tulisi optimoida hyödyntämällä koesuunnittelua ja vastepintamenetelmää.

Avainsanat	mukonihappo, nylon, prosessikehitys, biomuovit, GC, NMR, panosreaktori, jatkuvatoiminen reaktori

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Nylon is an important plastic which has numerous applications in many industries. It is mainly produced from petrochemical derivatives. Even though petrochemical free routes exist for the nylon production, these routes are in their infancy and have problems which make them less favoured than the petrochemical routes. This thesis was made for Technical Research Centre of Finland for a commercialisation project funded by Tekes.

The aim of this work was to develop the process of producing a derivative for a bio based nylon production. The project was started by conducting experiments with batch reactors to test if the reactors have affected the experiment results before the thesis. Process development was carried out by performing experiments with a continuous reactor and using the knowledge gained from the earlier batch reactor experiments. The reactions products were analysed mainly with a GC-FID, but a GC-MS and a NMR were also applied in this thesis.

The batch reactor experiment results revealed that most of the batch reactors had been affecting the past reactions. The experiments on working reactors should be redone to ensure the repeatability of the reactions. The continuous reactor experiments showed encouraging results and provided detailed knowledge about the process, despite the last four experiments which had problems with the raw material. It was discovered that more experiments should be conducted with the continuous process in the future before the process scale up. The process should be optimized by utilizing the Design of Experiments de-sign and the response surface method.

Keywords	muconic acid, nylon, process development, bio-plastics, GC, NMR, batch reactor, continuous reactor

Table of contents

Abbreviations

1 Introduction 1

1.1 Nylon 1
1.1.1 Production of nylon 1
1.2 Bio-plastics 2
1.2.1 C 3
1.2.2 Production of C 3
1.3 VTT route for C production 4
1.3.1 Technical Research Centre of Finland Ltd 4
1.3.2 VTT route 4
1.3.3 Hydrodeoxygenation 4
1.4 Scope of the work 5

2 Analysis equipment 6

2.1 Gas chromatography 6
2.1.1 GC-FID 6
2.1.2 GC-MS 7
2.2 Nuclear magnetic resonance 7

3 Batch reactor experiments 8

3.1 Materials 8
3.1.1 The reactors 8
3.1.2 Experiment set up 9
3.1.3 Chemicals 9
3.2 Batch reactor method 10
3.2.1 Method 10
3.2.2 Analysis method 10
3.3 Results 11
3.3.1 Reactor i 11
3.3.2 Reactor ii 11
3.3.3 Reactor iv 12
3.3.4 Reactor ii retest 12
3.3.5 Reactor iv retest 13

3.4 Discussion 13

4 Continuous reactor experiments 14

4.1 Materials 15
4.1.1 Continuous reactor 15
4.1.2 Experiment set up 15
4.1.3 Chemicals 16
4.2 Continuous experiments method 17
4.2.1 Method 17
4.2.2 Analysis 18
4.3 Results 18
4.3.1 Test 1: Raw material flow rate 15 g/h 18
4.3.2 Test 2: Raw material flow rate 30 g/h 19
4.3.3 Test 3: Raw material flow rate 60 g/h 20
4.3.4 Test 4: Raw material flow rate 7 g/h 22
4.3.5 Test 5: Catalyst changed to F 23
4.3.6 Test 6: Catalyst activation 24
4.3.7 Test 7: Solvent changed to Y 25
4.3.8 Test 8 Y retest 25
4.3.9 Test 9: Recycling reactor 26
4.3.10 Test 11: Concentration increase 28
4.4 Discussion 29

5 Conclusions 32

References 35

Appendices

Appendix 1. Reactor i GC-FID
Appendix 2. Reactor ii GC-FID
Appendix 3. Reactor iv Fraction 1 GC-FID
Appendix 4. Reactor iv Fraction 2 GC-FID
Appendix 5. Reactor ii Retest GC-FID
Appendix 6. Reactor iv Retest GC-FID
Appendix 7. Continuous experiment 1–6: Raw material
Appendix 8. Continuous experiment 1: Sample 1
Appendix 9. Continuous experiment 1: Sample 2
Appendix 10. Continuous experiment 1: Sample 3
Appendix 11. Continuous experiment 1: Sample 4

Appendix 12. Continuous experiment 1: Sample 5

Appendix 13. Continuous experiment 2: Sample 1

Appendix 14. Continuous experiment 2: Sample 2

Appendix 15. Continuous experiment 2: Sample 3

Appendix 16. Continuous experiment 2: Sample 4

Appendix 17. Continuous experiment 2: Sample 5

Appendix 18. Continuous experiment 2: Sample 6

Appendix 19. Continuous experiment 3: Sample 1

Appendix 20. Continuous experiment 3: Sample 2

Appendix 21. Continuous experiment 3: Sample 3

Appendix 22. Continuous experiment 3: Sample 4

Appendix 23. Continuous experiment 3: Sample 5

Appendix 24. Continuous experiment 3: Sample 6

Appendix 25. Continuous experiment 4: Sample 1

Appendix 26. Continuous experiment 4: Sample 2

Appendix 27. Continuous experiment 4: Sample 3

Appendix 28. Continuous experiment 4: Sample 4

Appendix 29. Continuous experiment 4: Sample 5

Appendix 30. Continuous experiment 5: Sample 1

Appendix 31. Continuous experiment 5: Sample 2

Appendix 32. Continuous experiment 5: Sample 3

Appendix 33. Continuous experiment 5: Sample 4

Appendix 34. Continuous experiment 5: Sample 5

Appendix 35. Continuous experiment 5: Sample 6

Appendix 36. Continuous experiment 6: Sample 1

Appendix 37. Continuous experiment 6: Sample 2

Appendix 38. Continuous experiment 6: Sample 3

Appendix 39. Continuous experiment 6: Sample 4

Appendix 40. Continuous experiment 6: Sample 5

Appendix 41. Continuous experiment 6: Sample 6

Appendix 42. Continuous experiment 8: Sample 1

Appendix 43. Continuous experiment 8: Sample 2

Appendix 44. Continuous experiment 8: Sample 3

Appendix 45. Continuous experiment 8: Sample 4

Appendix 46. Continuous experiment 8: Sample 5

Appendix 47. Continuous experiment 9: Sample 1

Appendix 48. Continuous experiment 9: Sample 2

Appendix 49. Continuous experiment 9: Sample 3
Appendix 50. Continuous experiment 9: Sample 4
Appendix 51. Continuous experiment 9: Sample 5
Appendix 52. Continuous experiment 10: Sample 1
Appendix 53. Continuous experiment 10: Sample 2
Appendix 54. Continuous experiment 10: Sample 3
Appendix 55. Continuous experiment 10: Sample 4
Appendix 56. Continuous experiment 10: Sample 5
Appendix 57. Continuous experiment 11: Sample 1
Appendix 58. Continuous experiment 11: Sample 2
Appendix 59. Continuous experiment 11: Sample 3
Appendix 60. Continuous experiment 8: Raw material
Appendix 61. Continuous experiment 9–10: Raw material
Appendix 62. Continuous experiment 11: Raw material
Appendix 63. Continuous experiments 8–11: Raw material before the experiments

Abbreviations

VTT	Technical Research Centre of Finland Ltd
HDO	Hydrodeoxygenation
GC	Gas chromatography
FID	Flame ionization detector
MS	Mass spectrometer
NMR	Nuclear magnetic resonance
DOE	Design of Experiments

1 Introduction

1.1 Nylon

Nylon is a family of synthetic polyamides which are invaluable plastics used in textiles, construction, medical and other applications. Apart from nylon 6 and nylon 6,6, nylon grades are mainly used in specialist applications. The first nylon (nylon 6,6) was first synthesized by Wallace Carothers at DuPont's research facility in 1935. Nylon 6 was produced by Paul Shlack from caprolactam in 1938. Several other resins of nylon with different properties have been developed and these include: nylon 6,10, nylon 6,12, nylon 11, nylon 12, Kevlar® and Nomex®. [1, p. 243; 2]

Nylon has a wide range of applications in many industries due to its versatility, toughness and thermal and chemical resistance. Nylons are mainly used to produce synthetic fibres which can be manufactured into carpets, clothing or rope. Nylons are widely used as engineering thermoplastics in injection molding. The automotive industry has, for example, increasingly started to replace some metallic parts with nylon. Nylon is also a common material in the electrical industry and nylon films are used as packaging in food industry. [1, p. 243–244; 2]

The annual production of nylon is over a million metric tons [3], and the production is increasing annually due to a growing demand of nylon based products. Nylon 6 and nylon 6,6 are the most produced nylons in the market. China is the leading nylon 6 producer in the world and the United States is the largest nylon 6,6 producer. [4]

1.1.1 Production of nylon

There are two methods to produce nylon: ether by a condensation reaction between diamine and dibasic acids or by a ring-opening polymerization of the lactam ring. The vast majority of nylon is produced from crude oil derivatives such as benzene, cyclohexane, phenol and toluene. These derivatives can be converted into caprolactam, which is an intermediate in nylon 6 production, or into an adipic acid which is used in the production of nylon 6,6. [1, p. 244; 2]

Nylon 6 is produced by the ring opening polymerization of caprolactam. A classic reaction pathway to synthesize caprolactam from cyclohexanone can be seen in figure 1. After reduction and oxidation, cyclohexanone is treated with hydroxylamine, which converts cyclohexanone into cyclohexanone oxime. This intermediate oxime is rearranged, into amide caprolactam in the presence of an acid catalyst in the Beckmann rearrangement. This process has drawbacks, however, since it requires multiple steps and vast amounts of ammonium sulphate are produced as a side product, e.g. one ton of caprolactam yields 4.5 tons of ammonium sulphate. 95% of caprolactam in the world is produced by this reaction. To avoid these problems other processes have been developed. These processes tend to avoid the formation of cyclohexanone oxime. [1, p. 258—264; 5, p. 1]

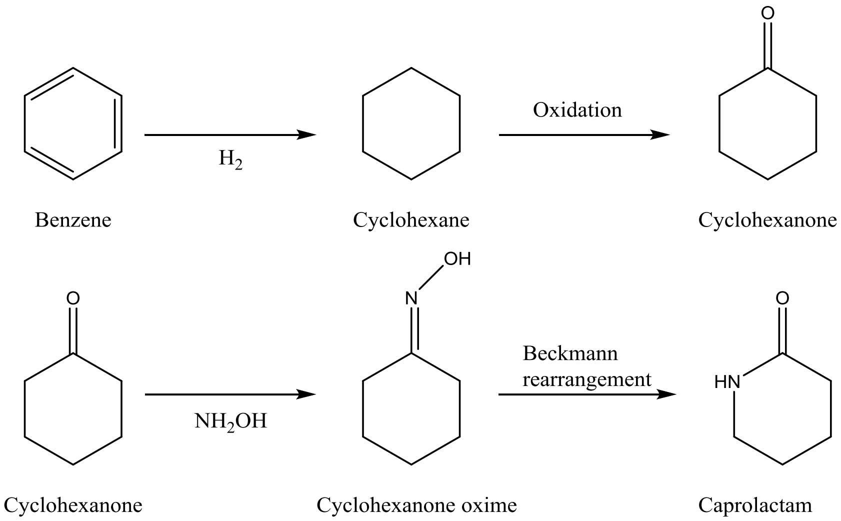

Figure 1. Reactions to convert benzene into cyclohexanone and cyclohexane into caprolactam

1.2 Bio-plastics

The plastic industry relies on petrochemical platform chemicals for most of its existence. The main problems with petrochemicals are that they are their finite and have detrimental effects on the environment. Due to increasing environmental regulations, the fluctuating oil price and increasing consumer demand for bio-based chemicals, plastic manufacturers have become increasingly interested in bio based plastics. These bio-plastics are plastics that are derived from renewable feedstock such as starch, cellulose, fatty acids, sugars, proteins, and other biological sources. They can be converted into monomers and polymers by microorganisms or chemical reactions. These monomers and polymers are often defined as platform chemicals since these molecules are used as building blocks to produce many valuable chemicals, for instance, succinic acid can be converted into valuable chemicals seen in figure 2. [6, p. 2082; 7, p. 21]

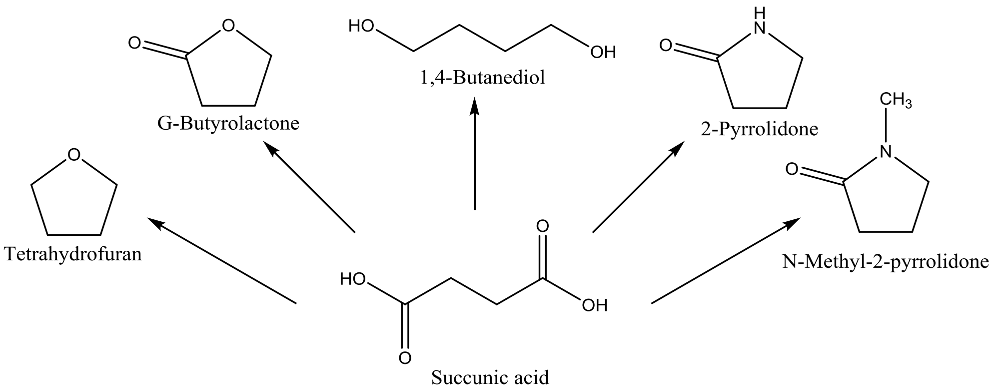

Figure 2. Possible derivatives of succunic acid [8, p. 23]

1.2.1 C

There has been a growing interest in the C, which is dicarboxylic acid, due to its potentiality to be used as a platform chemical for many bio-plastics. These include polyurethane and polyethylene terephthalate (PET) [7, p. 16]. Research has revealed that C could also be used to produce caprolactam, meaning that C could provide possible oil free route for the nylon 6 production [5].

C has three isometric forms, the trans,trans-C, cis,trans-C, and cis,cis-C. The reaction to produce caprolactam from C can be conducted in different ways depending on the isometric form. These isomeric forms can be converted in a two-step route. Firstly the C is converted in adipic acid with hydrogen and catalyst which is then catalytically reduced to capralactam with hydrogen and ammonia in the presence of catalyst. The reaction is high yielding, has fewer by-products and avoids sulphate formation produced from crude oil derivatives [5, p. 1, 7].

1.2.2 Production of C

C can be prepared chemically and microbiologically. In the chemical route, C is produced from either sugar petro-chemical feedstock in the presence of heavy metal catalysts [9, p. 3992-3993; 10, p. 615]. Microbiologically C can also be produced from aromatic compounds such as benzoate toluene, benzene and phenol. Some bacteria are able to convert these chemicals into catechol. Catechol 1,2-dioxygenase enzyme, for example, is able to catalyse the cleavage of the aromatic ring to produce C. [11; 10, p. 616] The problem with these processes is the crude oil feedstock, which means that they cannot be applied to the production of bio-nylon.

One route to make Muconic from renewable feedstock is by fermentation of d-glucose. The problem with this microbiological process is its low C yield. With the current technology, the achievable bio based C yield is 30 %. [10 p. 618, 621; 7, p. 22] Due to this problem, C is seen as a less attractive intermediate in caprolactam production than cyclohexanone. New technology would be needed to make the bio C route as efficient as petrochemical routes.

1.3 VTT route for C production

1.3.1 Technical Research Centre of Finland Ltd

Technical Research Centre of Finland Ltd (VTT) is the leading R&D centre for applied research in Northern Europe. It was founded in 1942. VTT develops scientific solutions, research and innovation services that enhance the competitiveness of companies, society and other customers as well as to create the prerequisites for society’s sustainable development, employment and wellbeing.[12]

1.3.2 VTT route

VTT has been developing routes to C since 2013, based on the selective catalytic hydrodeoxygenation of A. This method produces C, D and E from A or B [13]. VTT has already developed fermentation technology AGROBIO to produce A from pectin, making it possible to combine these technologies together for the production of bio nylon [14].

1.3.3 Hydrodeoxygenation

Hydrogenlysis is a reaction in which the addition of hydrogen cleaves carbon to carbon or carbon to heteroatom bonds. This heteroatom is commonly oxygen, nitrogen, sulphur or metal. Hydrodeoxygenation (HDO) is a hydrogenlysis reaction in which oxygen is cleaved from a compound. Cleaved oxygen forms by-product water with hydrogen gas. The HDO reaction has applications in biofuel production. For example fatty acids can be converted into fuel-like hydrocarbons with catalysed HDO. [15, p. 4678; 16]

HDO requires a catalyst, and often precious metals are used, for example F and G. The possible catalysts utilized in the reaction, have an ability to catalyse the HDO of epoxides and diols to alkenes in quite mild conditions. Firstly, F reacts with hydrogen to produce Fb. The alcohol solvent is essential to the activation of the catalyst where it interacts to form an intermediate. Fb cleaves the hydroxyl groups of A. This cleavage causes carbon-carbon double bond to form resulting in trans,trans-C [17. p. 9998-1000]. Theoretically this reaction can have a 100% yield, which would make the A HDO process more efficient than the competing biotech route.

1.4 Scope of the work

The work is part of a Tekes funded commercialisation project to make bio-nylon, with confidential results produced during the period of research. As such, aspects and certain details have been removed from the thesis to maintain an intellectual property right.

The production of platform chemicals from bio-based resources are in their infancy and it is often the case that bio-based processes are not as efficient as the petrochemical routes, leading to higher prices and therefore making them unattractive for commercialisation by industry. The focus is to take the bio based route and make it as efficient as the petrochemical route, both in terms of reaction efficiency and environmental impact.

VTT has been studying the catalysed HDO reaction to produce C by conducting experiments on pressure reactors, which are pressurized chemical reaction vessels. The results of the experiments have been good but unreliable; and the repeatability of results has not been achieved. The problems with reactions have raised an idea that reactors themselves have been affecting the reactions by poisoning the catalyst or catalysing different reactions [18]. In this thesis, the difference between three reactors with different coatings is actively determined.

The knowledge gained from the pressure reactor tests, is then directly applied to continuous reactor processes for the first time. The work includes the optimization of continuous process conditions. The current reaction process has a yield is of approximation 20–65 %. The aim is to increase this to a stable 80–90%. The novelty of this work is that by moving to a continuous flow reactor, the reaction times can be systematically reduced and a high reactor throughput is achieved. Such a novel process has not been reported in the scientific literature and thus a novel intellectual property (patent) can be obtained if successful.

2 Analysis equipment

2.1 Gas chromatography

In this work gas chromatography (GC) was employed in the analysis of reaction products. With chromatography it is possible to detect amounts of known and unknown compounds in a sample. As in all forms of chromatography, GC has a stationary and a mobile phase. The mobile phase, in this case is a carrier gas, moves the sample through the stationary phase, the column, where the sample components interact with the column differently which causes them to move through the column with different rates. As the components arrive at the end of column, they are sensed by the detector. The carrier gas has to be inert and it should not be capable of absorbing into the column wall. The usual carrier gas is helium, but hydrogen and nitrogen are also used in special applications. Two different gas chromatographs were used in thesis: GC-FID and GC-MS. [19, p. 3–4; 20, p. 17–18]

2.1.1 GC-FID

GC-FID is a gas chromatograph that utilizes a flame ionization detector (FID) which is one of the most used GC detectors. After the sample exits the column, it is burned in a hydrogen flame which releases ions. The detector senses compounds by measuring an electric current caused by the released ions. [19, p. 3–4; 20, p. 29–31]

2.1.2 GC-MS

GC-MS is a combination of gas chromatograph and mass spectrometer (MS). It was used to study unknown spikes in GC-FID analysis. The mass spectrometer is not only able to provide quantitative information but also knowledge about the structure of the sample. MS consists of an ion source, an analyser and a detector. When the separated sample compound enters the mass spectrometer, it is ionized in the ion source. The gas ion fragments are accelerated with an electric field and move to the magnetic analyser. The trajectory of ion fragments is curved by the magnetic field of analyser. The ion fragments with more mass will have a smaller radius than the lighter fragments. The analyser separated the ions depending on their mass to charge ratio. After the analyser, the fragments will strike the detector which measures the mass-to-charge ratio of the ion fragments. [19, p. 3, 9–10; 20, p, 32–33]

2.2 Nuclear magnetic resonance

A nuclear magnetic resonance (NMR) spectroscopy was used to analyse a solid material in synthesized raw material. NMR is possibly the most important form of spectroscopic analysis. It is commonly used to determine the structure of organic molecules. The instrument produces a magnetic field, which interacts with nuclei which have a spin property. The nuclei which possess the spin property have unpaired proton or neutron, for example ^{1}H and ^{13}C. They act like magnets when placed into the magnetic field and line up according it. The nuclei can line up parallel or anti-parallel to the magnetic field. These two orientations do not have the equal change to occur because they do not possess the same energy. The anti-parallel orientation has more energy than the parallel. When the nuclei with parallel orientation are hit with a pulse of electromagnetic radiation, they are able to flip to the higher energy anti-parallel orientation. This means that the nuclei are resonating. Different species of nuclei have a different resonance frequency, meaning that they can be characterised by the detector, which detects the intensity of the absorption with different frequencies. The intensity of the absorption describes the abundance of the specific nuclei in the sample. [21; 22 p. 1–22]

3 Batch reactor experiments

The benefit of pressurized reactors is that reactions can be conducted at higher temperatures than the boiling point of the solution. The increased temperatures are able to make reaction rates quicker than in unpressured reactions. This temperature effect on the reaction rate can be seen on the Arrhenius equation

$$\mathrm{k} = \mathrm{A}e^{\frac{-\mathrm{E_a}}{\mathrm{RT}}}, \qquad (1)$$

where k reaction rate coefficient, A is pre-exponential factor, E_a is activation energy of reaction, R is the gas constant and T is temperature. If the temperature increases, the reaction rate coefficient should increase as well. Generally, a 10 °C temperature rise will double the reaction rate. Also according to the collision theory, the number of successful collisions increases with the rise of concentration. When the pressure is increased, the concentration of gas increases and thus the reaction rate becomes faster. [23, p. 6–7; 24, p. 101]

The pressure vessels used in the experiments are batch reactors. Batch reactors are closed systems. This means that nothing is added or removed from a reactor while a reaction is occurring. When the reaction is complete, products are then removed and the reactor is cleaned. Versatility is the principal benefit of batch reactors. One reactor is suitable for different reactions and product grades. They are flexible to operate and can be easily shutdown if necessary. Reactors can be cleaned and made sterile easier than other reactor types. Due to these benefits, batch reactors are commonly used to study new chemical reactions. [25, p. 10, 663]

3.1 Materials

3.1.1 The reactors

VTT has done experiments with four different pressure reactors, each with a different coating. These reactors can be seen in figure 3. Reactor i is a stainless steel reactor with a damaged chemical resistant coating of AR229 PFA Ruby Red which is perfluoro alkane polymer. The reaction mixture and the stainless steel wall of the reactor are in contact during the reaction, which means that it could possible for the steel to affect the reaction.

Reactor ii has a bulky and heavy head. Its coating is also AR229 PFA Ruby Red. The coating is non-stick and highly chemical resistant. Reactor iv has a removable Teflon cup as a reaction vessel. At the bottom of Teflon cup, there is an unknown black material which could not be removed. The material could be able to affect the reaction. The chemical resistant coating of reactor ii should possess better chemical resistant qualities than Teflon has. Reactor iii is also a Teflon reactor. It was not examined to save time because it was very similar to the reactor iv.

Figure 3. Reactors i, ii and iv

3.1.2 Experiment set up

The reactors were heated by immersing them in a silicon oil bath, which was heated by a lab hot-plate. The temperature of the oil bath was controlled with the hot-plate’s temperature program which measured the bath temperature with a thermocouple. The reactor temperature was measured also using a thermocouple. The agitation of the reaction mixture was carried out with a magnetic cross stirrer rotated by the lab hot plate.

3.1.3 Chemicals

Chemicals used in batch reactor experiments were all supplied by Sigma-Aldrich and used without further purification.

3.2 Batch reactor method

Reaction parameters were determined from VTT's earlier pressure reactor experiments [13]. It was discovered that the optimum reactions conditions at the present time are with temperatures ~ 130 °C and pressure ~ 500 kPa in X solvent and F catalyst and M co-catalyst.

The reactor products were analysed using GC-FID. The samples were prepared by silylation of the hydroxyl group, which is done to increase the volatility of a molecule. This allows GC to produce more accurate results. [26, p. 4]

3.2.1 Method

The pressure vessel was charged with A (1 g), M (100 mg) and F (119 mg). Before the reactor was sealed, X (10 ml) and magnetic stirrer were added. The vessel was then purged twice with nitrogen gas and subsequently three times with hydrogen to 500 kPa. The Reactor was then heated in an oil bath (130 °C) to give an internal temperature of 118—123 °C. The reactor was then maintained at this temperature for 48 hours after which it was cooled to room temperature and vented to atmospheric pressure. The reaction product was washed from the reactor two times with 11 ml of Y. The product filtered under vacuum using porosity a 3 glass filter. The brown filtrate was transferred into an evaporator flask. The solvent was removed from filtrate under vacuum using a rotary evaporator (<2 kPa, 45 °C) and then left to a vacuum oven (5 kPa, 40 °C) overnight. Once dry the yield of crude material was obtained.

The experimental method was described for the reactor ii. The experiments were conducted using the above method utilizing the different batch reactors. The reactor ii and the reactor iii with a new Teflon cup were also retested.

3.2.2 Analysis method

A sample of the material (5—10 mg) was weighed into a glass vial. Acetone (0.4 ml) and pyridine (0.4 ml) were added into the vial and then K (0.2 ml). The vial was then heated in a block heater to 60 °C for 30 min.

GC-FID analyses were carried out using an Agilent 6890 equipped with a FID: Column & length: HP-5 5% Phenyl Methyl Siloxane, 30 m, 0.32 mm, 0.25 um film, carrier gas: He, injector temperature: 250 °C, FID temperature: 300 °C, oven temperatures: Initial temp: 30 °C, Initial time: 1.00 min, Ramp: 13 °C/min to 300°C, final time 15 min. GC results were compared to reference standards, which were used to accurately determine the products obtained in the experiments.

3.3 Results

3.3.1 Reactor i

Reactor i product had an appearance of light brown solid with visible white particles after the vacuum oven drying. The end weight of the product was 1.1425 g. A sample (6.3 mg) was weighed for an GC-FID analysis. The amounts of compounds can be seen on table 1.

Table 1. Reactor i GC-FID results

Name	m-%	m (mg)
B	28.6	32.667
A	29.7	33.877
C	11.2	12.785
D	30.6	34.922

3.3.2 Reactor ii

Reactor ii product appearance was black oil. The product’s weight was 1.2198 g. The weighed sample’s weight was 9.3 mg. The result of the GC-FID analysis can be seen in table 2

Table 2. Reactor ii GC-FID results

Name	m-%	m (mg)
B	6.004	7.324
A	5.533	6.749
C	19.693	24.021
D	68.770	83.886

3.3.3 Reactor iv

The reactor products were in two fractions. Fraction 1 was a yellow transparent liquid which had evaporated into light brown solid. and the fraction 2 was white solid crystals. Fraction 1 was produced: 0.8437 g and fraction 2: 0.3631 g. and the total weight: 1.2068 g. For GC-FID, sample of fraction 1 (9.2 mg) and fraction 2 (6,8 mg) was prepared. GC-FID results for fraction 1 can be seen in table 3 and for fraction 2 in table 4.

Table 3. Reactor iv fraction 1 GC-FID results

Name	**m-%**	**m (mg)**
B	52.076	43.936
A	10.362	8.742
C	15.219	12.840
D	22.343	18.851

Table 4. Reactor iv fraction 2 GC-FID results

Name	**m-%**	**m (mg)**
B	71.931	26.118
A	27.514	9.990
C	0.000	0.000
D	0.555	0.201

3.3.4 Reactor ii retest

Reactor ii product appearance was brown solid. The final product weight was 1.1874 g. The weight of the sample prepared for GC-FID was 6.4 mg. The results can be seen in table 5

Table 5. Reactor ii retest GC-FID results

Name	**m-%**	**m (mg)**
B	23.952	28.440
A	10.537	12.512
C	15.504	18.409
D	50.008	59.379

3.3.5 Reactor iv retest

The product's appearance was a brown solid. The product's weight was 1.4447 g. and the GC-FID sample weight 5.4 g. The results are shown in table 6

Table 6. Reactor ii retest GC-FID results

Name	m-%	m (mg)
B	66.231	0.957
A	4.340	0.063
C	6.986	0.101
D	22.443	0.324

3.4 Discussion

The purpose of these experiments was to test the effects of the reactors on the VTT's earlier experiments. The GC-FID analysis of reactor i product shows that some C has been produced, but large amounts of raw material were left unreacted. The appearance of the product was light brown solid but some white solid could be seen in the product. White solid was, according to the analysis, unreacted material. The product of Reactor ii was much darker and oilier than the reactor i product. The analysis of the reaction mixture indicates to have produced a significant amount of C and D with an almost total consumption of raw material. Reactor iv products were in two fractions: solid white crystals and yellow liquid. Characterisation by GC-FID shows that the crystals were raw material. Only a little C had been formed in reaction according to the analysis of liquid fraction. Due to reactor ii results, reactor ii was retested. The results of the retest were significant in that they were not as good as the results of the first test. Less raw material had reacted and the product was not as oily. Reactor iv was tested with a new Teflon cup to find out whether the black material imbedded in/on the Teflon or reaction vessel material itself is the reason for the reactor failure. The appearance and the GC-FID results show that reactor iv did produce better results than the first reactor iv test did, but a high amount of raw material has been left unreacted.

GC-FID analyses show that reactors i and iv did not produce good results compared to reactor ii products and VTT's earlier experiments and it would seem that these reactors could have been affecting VTT's earlier reactions. The reasons for reactor i results were the most likely caused by contamination on the stainless steel wall or dirt on the surface of damaged chemical resistant coating. Reactor iv retest showed the contamination was the most likely reason for the reaction failure, however the reaction still had a large amount of unreacted material, thus it might be that Teflon is affecting the reaction. The colour of the reaction products seems to be a good indicator of the quality of product. The darker and oilier products are shown to indicate good production of C and D.

It should be noted that the pressure gauges of all the reactors were not befitting for pressure ranges used in reactions. This was especially with reactor iv, the where pressure gauge could not be used for accurate measuring. However, the charging of hydrogen was undertaken accurately with a gauge range 0-2000 kPa that was mounted to the wall during initial pressurization. During the reactor ii experiment, reactor heating was noticed to be slow compared to reactor i. The reason was discovered to be the heavy head of the reactor, which was acting as a heat gradient and was slowing the heating process. The problem was solved by lagging the reactor with insulation. This could have caused some reaction problems with VTT’s past experiments. An unexplained pressure rise could be seen on the second day of reactor ii reaction, but not with retest. It could be possible that there was a problem with the pressure gauge or unknown reaction occurred in the reactor, but this was not investigated further. During reactor ii retest, it was also noticed that the reactor gauge showed 200 kPa higher pressure than the gauge of the inlet that was used to pressurise the reactor.

4 Continuous reactor experiments

Continuous reactors are more favoured in chemical industry than batch reactors. In a continuous process, the reactants are added into the reactor and the products are removed continuously. They are capable of producing large quantities of the same product with static quality, because conditions within the reactor can be made constant. Continuous reactors are not as versatile as batch reactors but offer a more cost effective solution for large scale production, due to lesser requirement for labour force and cheaper operation costs. [25, p. 10, 663]

The continuous reactor used in this work is a trickle-bed reactor which is a gas-liquid-solid reactor. The solid catalyst is fixed in a packed bed inside of the reactor. The liquid is flowed downwards through the catalyst bed. The gas is usually flowed with liquid, but counter current is also viable. The trickle bed reactors are commonly used in hydrodesulphurization, and hydro cracking. [27, p. 373]

4.1 Materials

4.1.1 Continuous reactor

The reactor used to study the continuous process is a sulphuric free tube reactor. The reactor is 30 cm long and has a diameter of 12 mm. The catalyst bed held with-in the reactor, is supported by a metal rod. The reactor, the metal rod and fasteners can be seen in figure 4.

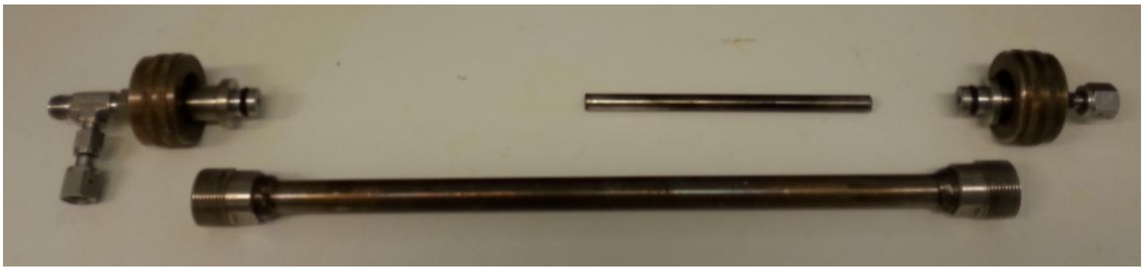

Figure 4. The tube reactor, the metal rod and the fasteners

4.1.2 Experiment set up

The raw material in a solution is drawn into the system with a HPLC pump with the mass flow rate monitored using a balance under the raw material vessel. Before the reactor, the raw material flows through a pre-heater vaporizer and is mixed with the gas flow. The system is capable of using hydrogen, nitrogen and argon gasses. The volumetric flow of the gases is controlled with flow controllers. The reactor heating is done using two 230 V ceramic electronic ovens. The reactor temperature is measured with thermocouple which measures the temperature from three points in the reactor. After the reactor, the products enter the pressurized sampling vessel, where the products can be collected under pressure. The products then enter the pressure controller and after that the sampling vessel. In this work, the products were collected using the second sampling vessel. The both sampling vessels are cooled down using a cryostat. The used gas continues from the sampling vessel and to FTIR or an air conditioner. The reactor system diagram is illustrated in figure 5.

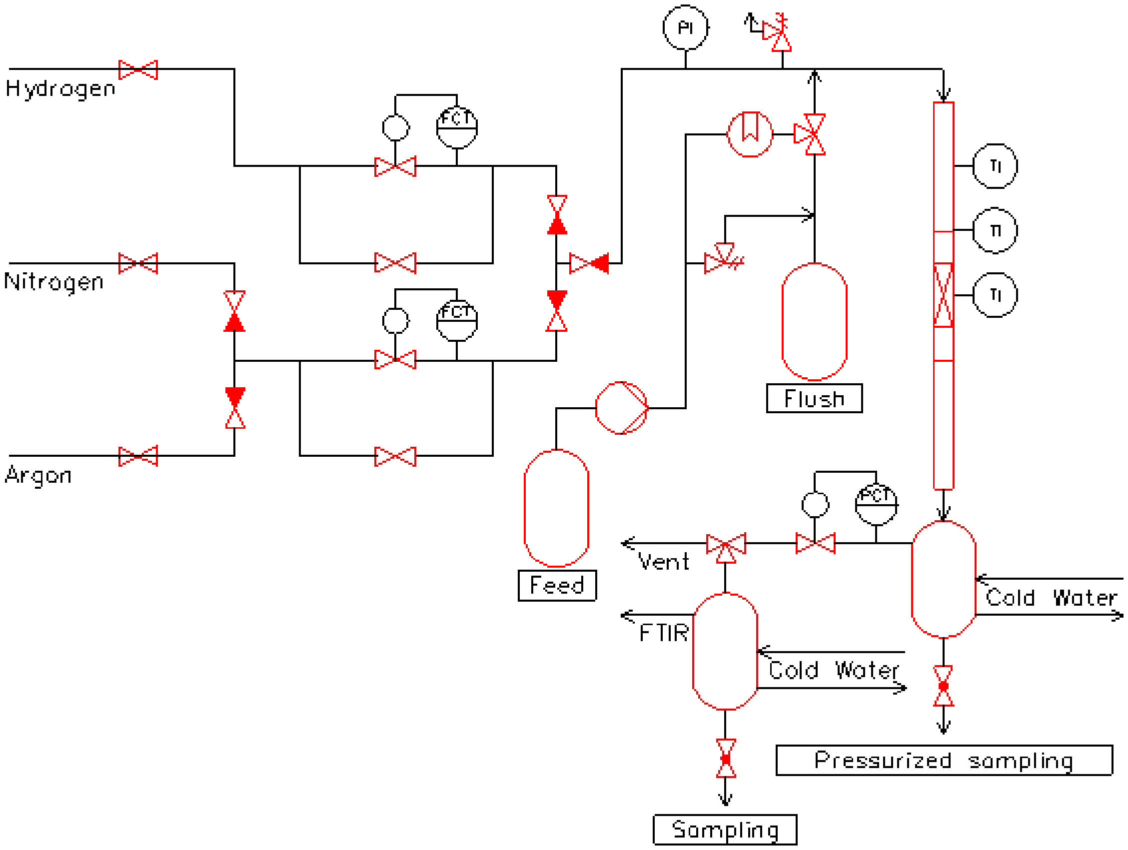

Figure 5. The continuous reactor system

4.1.3 Chemicals

All the chemicals were supplied by Sigma-Aldrich, except B, coarse J and quartz wool. J was supplied by Alfa Aesar, quartz wool by Roth and B was produced in house by the VTT. During the project, more of the raw material, B, had to be synthesised with esterification of I and X in the presence of H_2SO_4. The product was oily B and solid material which had to be filtered with porosity 3 glass filter. The NMR analysis showed the solid material to be unreacted I.

4.2 Continuous experiments method

The experimental conditions were similar to the conditions from the batch reactor experiments. Due to A being highly insoluble, a 0.1 g/ml B in X solution was used instead as a raw material. The catalyst was changed from F to G, due to significantly lower catalyst costs and more material required for the continuous reactor. The catalyst bed also consisted of inert J to spread the bed to increase the bed height Changing the solvent from X to Y was studied, since it would decrease the process costs and make the process a truly petrochemical free route for C production. Initially in Y tests, H was to be used as a raw material, but it was not soluble enough in Y, meaning B from had to be used.

The samples were analysed using the same method in the batch reactor analysis, however because of the X in reaction mixture, acetone was decided not to be added in sample preparation.

4.2.1 Method

The catalyst bed, consisting of G (0.83 g) and coarse J (2.49 g) between quartz wool layers (1 g), was placed into the reactor which was then attached into the process system. The reactor ovens were then left to heat up to 140—155 °C and the reactor to ~130 °C. After the heating was complete, the reactor was pressure tested with argon gas by increasing the system pressure into 500—1000 kPa. The reactor was then pressurized into 500 kPa with hydrogen and the hydrogen flow through the reactor was set to 5 l/h. The experiment was started by setting pump raw material feed to 15 g/h and the heating of pre-heater to 115 °C. A sample was collected from the product trap every hour. The reactor was stopped after 6 hours by closing the pump, the hydrogen feed and the heating. The reactor was then depressurised and it was set to have a 50 l/h nitrogen flow thought it. The end sample was collected ~15 h later.

The method was described for the test 1: 15 g/h raw material flow. The other experiments that were performed are shown in table 7.

Table 7. Continuous reactor experiments

Test #	Aim
1	Raw material flow rate 15 g/h
2	Raw material flow rate 30 g/h. Sampling was done every 30 min.
3	Raw material flow rate 60 g/h. Sampling was done every 15 min.
4	Raw material flow rate 7 g/h
5	The catalyst changed from G to F (0.77 g) and P-TSA (0.53 g).
6	The catalyst activated 1 h before the experiment with X and hydrogen flow.
7	Solvent changed to Y. Pressure increased into 1000 kPa, due to volatility of Y. Reactor heating was decreased into 135 °C
8	Test 7 retest. Pressure increased to 2000 kPa
9	Recycling system. The products were collected to raw material vessel and was left to run for 24 h.
10	Catalyst loading increased: G (4.15 g) and coarse J (20.75 g)
11	Increased concentration to 0.2 g/ml

4.2.2 Analysis

See sections 3.2.2 and 4.2.

4.3 Results

4.3.1 Test 1: Raw material flow rate 15 g/h

GC-FID results can be seen in table 8.

Table 8. GC-FID results of continuous reactor test 1

Test 1	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	5.6175	2.5	8.92	5.155
2	4.3075	2.43	12.3175	7.0175
3	4.21	2.305	11.3775	7.0025
4	4.205	2.2725	10.635	6.73
5	4.015	2.3225	10.4775	7.005

Figure 6 shows the GC-FID results as a line chart.

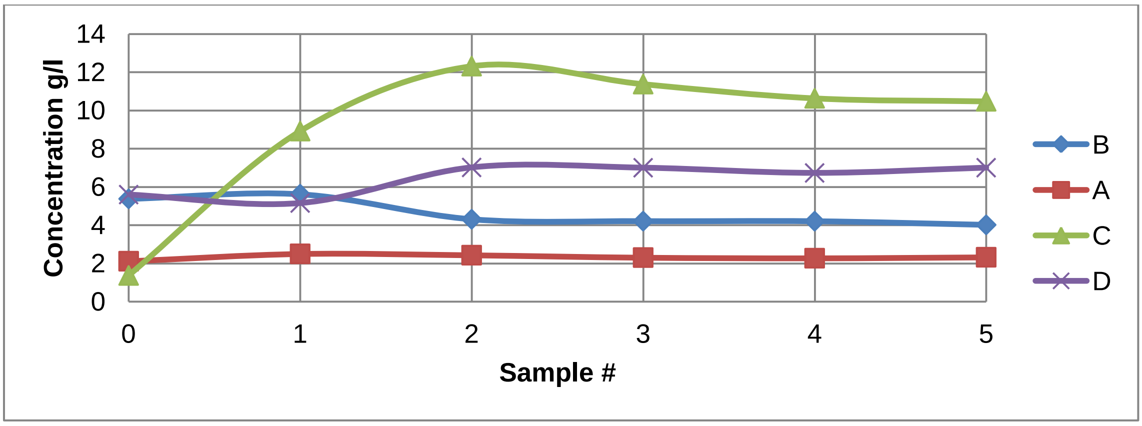

Figure 6. Line chart of continuous reactor test 1

The first reaction mixture sample has an appearance of dark brown transparent solution. The samples 2–4 were dark brown or almost black. The sample 5 was slightly lighter than the samples 2–4. The reaction mixtures are shown in figure 7. Some oil can be seen in the samples.

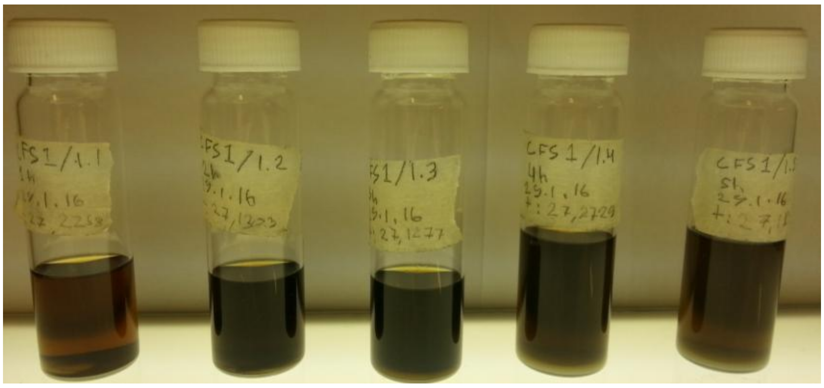

Figure 7. Test reaction mixture samples

4.3.2 Test 2: Raw material flow rate 30 g/h

GC-FID results can be seen in table 9.

Table 9. GC-FID results of continuous reactor test 2

Test 2	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	2.165	2.4275	9.1525	6.415
2	1.5825	2.2275	7.4475	6.5275

3	2.225	2.1625	7.7825	6.3825
4	2.2275	2.235	8.3425	6.6225
5	2.3775	2.27	8.8275	6.845
6	3.4375	2.3675	8.735	6.705

Figure 8 shows the GC-FID results as a line chart.

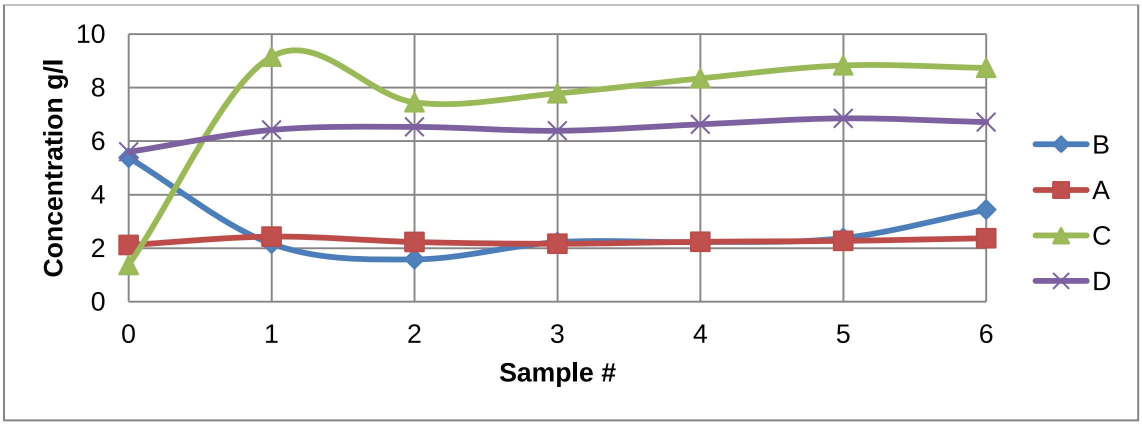

Figure 8. Line chart of continuous reactor test 2

The first two products were dark coloured, and they resemble the test products. The samples 3–6 have the same yellow transparent liquid colour. The samples can be seen in figure 9.

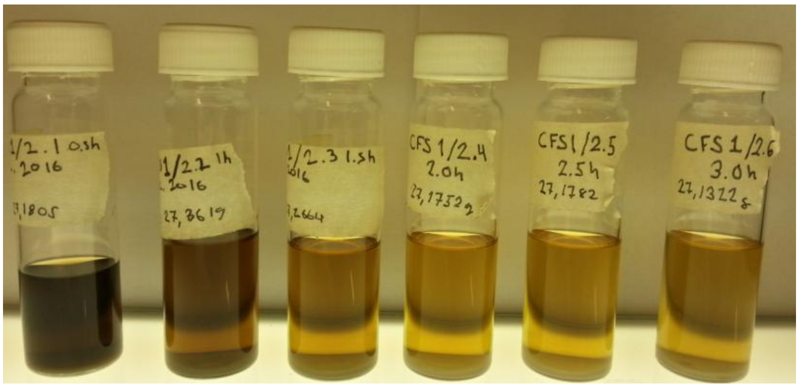

Figure 9. Test 2 reaction mixture samples

4.3.3 Test 3: Raw material flow rate 60 g/h

GC-FID results can be seen in table 10.

Table 10. GC-FID results of continuous reactor test 3

Test 3	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	3.525	2.685	13.0175	7.47
2	2.145	2.4375	10.17	7.45
3	2.1575	2.285	7.9025	6.96
4	2.77	2.3875	8.4	7.1175
5	2.345	2.39	8.7075	7.2625
6	2.7275	2.3875	8.79	7.005

Figure 10 shows the GC-FID results as a line chart.

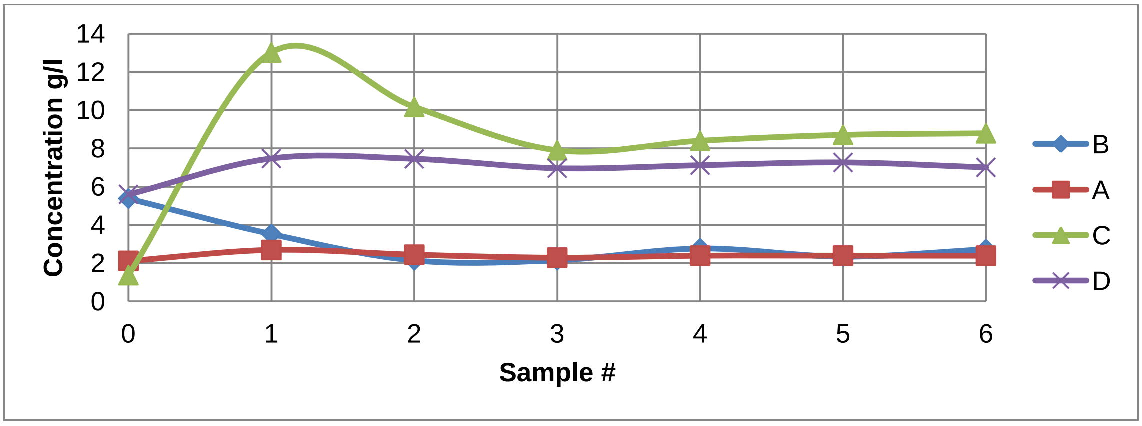

Figure 10. Line chart of continuous reactor test 3

The product appearance is very similar to experiment 2 samples 3-6. The sample can be seen in figure 11.

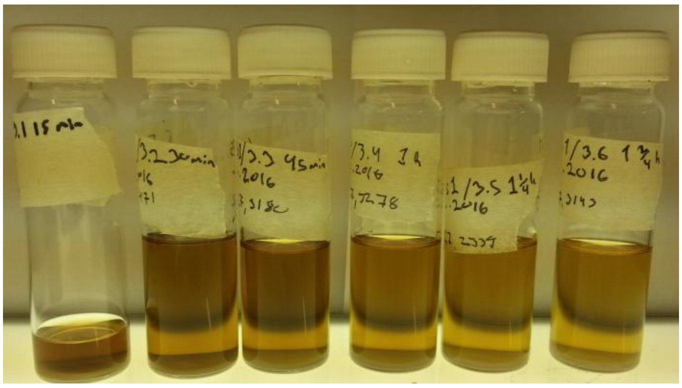

Figure 11. Test 3 reactor mixture samples

4.3.4 Test 4: Raw material flow rate 7 g/h

GC-FID results can be seen in table 11.

Table 11. GC-FID results of continuous reactor test 4

Test 4	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	3.2175	1.2325	2.8775	2.35
2	7.135	2.4875	15.285	7.1825
3	8.3125	2.7325	15.15	7.8025
4	8.5025	2.5	15.2925	7.4325
5	8.1025	2.575	12.765	7.0525

Figure 12 shows the GC-FID results as a line chart.

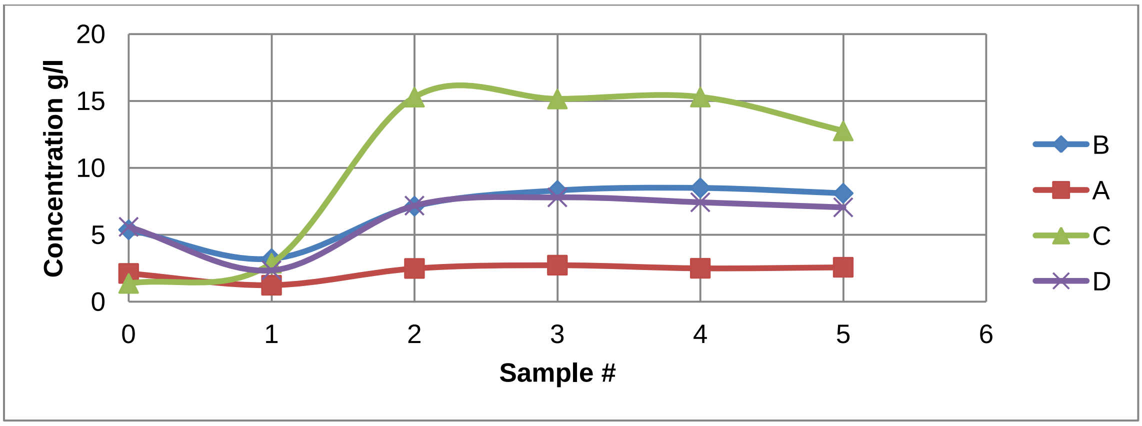

Figure 12. Line chart of continuous reactor test 4

The appearance of the samples was lighter than the appearance of the experiment products. These samples can be seen in figure 13.

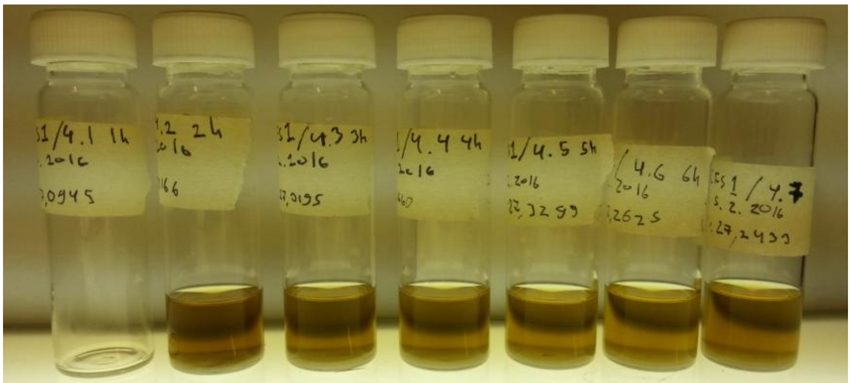

Figure 13.	Test 4 reactor mixture samples

4.3.5 Test 5: Catalyst changed to F

GC-FID results can be seen in table 12.

Table 12.	GC-FID results of continuous reactor test 5

Test 5	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	2.52	1.555	23.3025	18.455
2	1.9425	2.2175	21.7525	9.1
3	1.7275	2.1075	13.0875	6.71
4	2.115	2.1325	7.74	6.455
5	3.315	2.2575	6.38	6.7725
6	4.3625	2.225	4.935	6.305

Figure 14 shows the GC-FID results as a line chart.

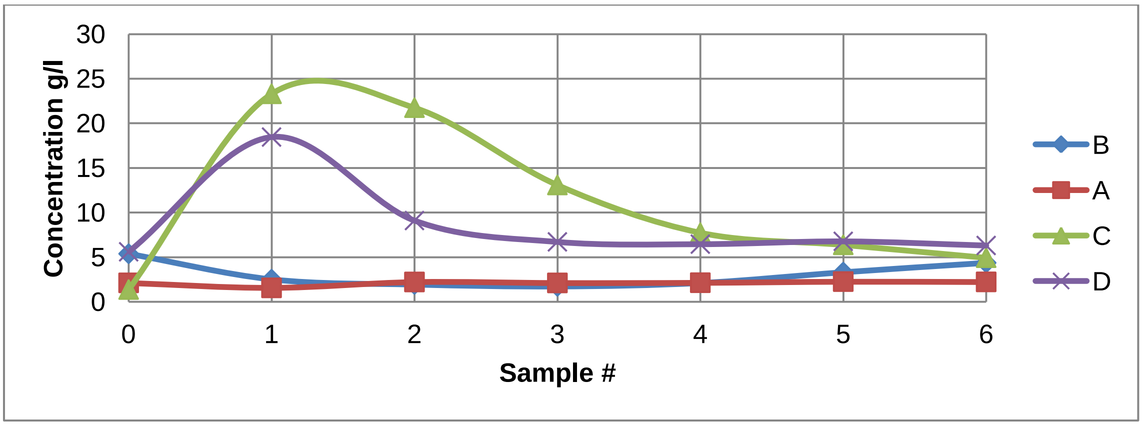

Figure 14.	Line chart of continuous reactor test 5

The first samples are very dark coloured. After the second sample, the sample colour becomes lighter. The samples can be seen in figure 15.

Figure 15. Test 5 reactor mixture samples

4.3.6 Test 6: Catalyst activation

GC-FID results can be seen in table 13.

Table 13. GC-FID results of continuous reactor test 6

Test 6	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	5.3775	2.115	1.37	5.5975
1	1.5425	0.895	2.925	2.0825
2	0	0.0675	0.29	0.54
3	5.03	2.335	12.98	7.9375
4	6.1225	2.96	12.8225	8.175
5	6.17	2.865	10.995	7.7775
6	6.3675	2.8775	10.625	7.655

Figure 16 shows the GC-FID results as a line chart.

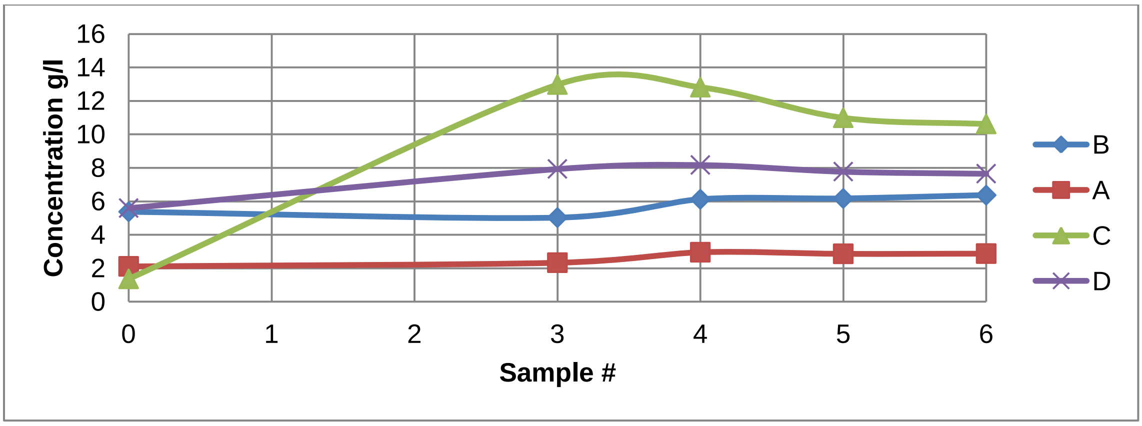

Figure 16. Line chart of continuous reactor test 6

The appearance of the products was very similar to the products in experiments 2 and 3. The second sample was colourless. The samples can be seen in figure 17

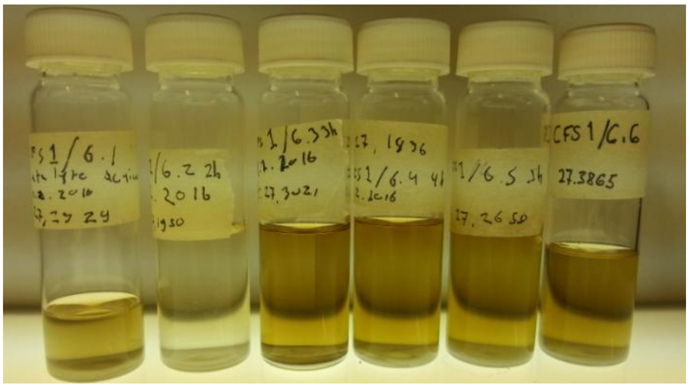

Figure 17. Test 6 reactor mixture samples

4.3.7 Test 7: Solvent changed to Y

The experimentation failed due to broken pressure controller.

4.3.8 Test 8 Y retest

GC-FID results can be seen in table 14.

Table 14. GC-FID results of continuous reactor test 8

Test 8	**Component concentrations (g/l)**

Sample #	**B**	**A**	**C**	**D**	**E**
0	7.735	1.045	3.825	33.645	0
1	0	0	0	0	0
2	0.1525	0.15	5.515	2.9075	3.265
3	0.505	0.665	8.6925	9.4875	1.6225
4	1.4925	1.14	8.4825	9.5275	1.4075
5	1.4925	1.14	8.4825	9.5275	1.4075
6	2.1875	1.38	8.0925	9.7625	1.2925

Figure 18 shows the GC-FID results as a line chart.

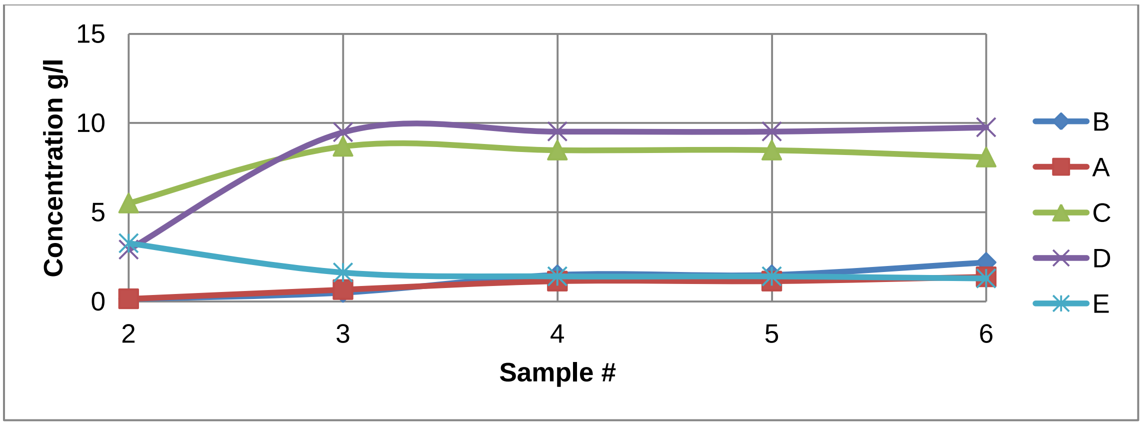

Figure 18. Line chart of continuous reactor test 8

All products, except the first sample, had the same appearance with the raw material. The product mixtures can be seen in figure 19.

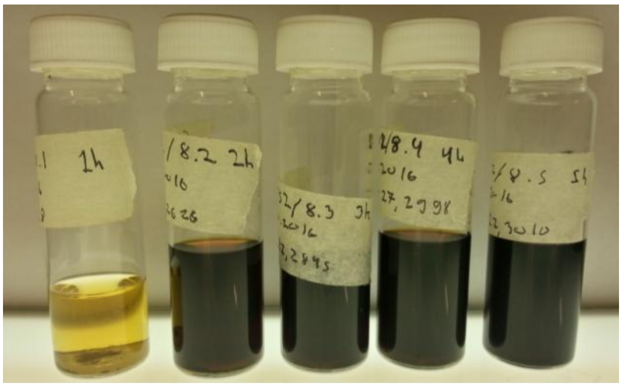

Figure 19. Test 8 reactor mixture samples

4.3.9 Test 9: Recycling reactor

GC-FID results can be seen in table 15.

Table 15. GC-FID results of continuous reactor test 9

Test 9	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	8.5975	1.7225	3.79	36.2975
1	7.05	2.9425	10.5175	39.02
2	8.0475	2.72	9.295	41.635
3	9.37	2.655	7.6425	45.32
4	10.9075	2.7575	6.79	48.0725
5	13.275	3.0975	7.1025	42.43

Figure 20 shows the GC-FID results as a line chart.

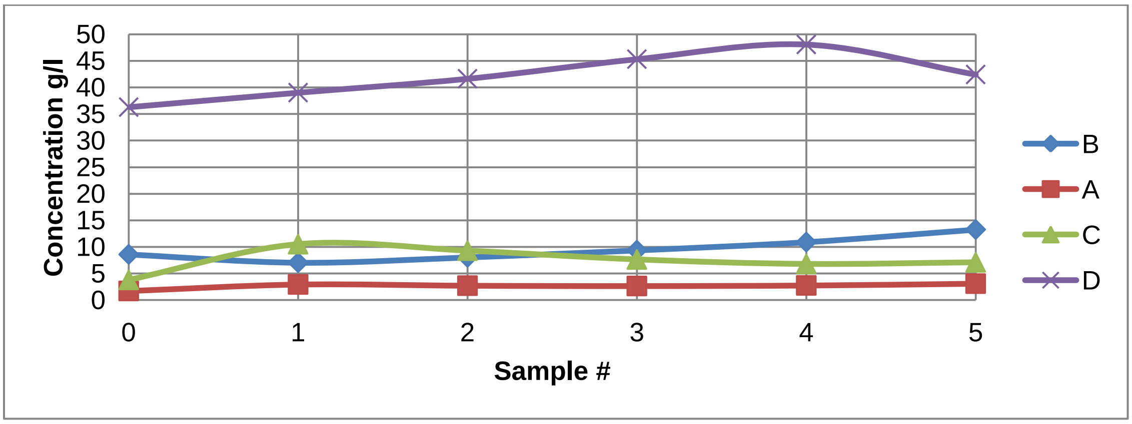

Figure 20. Line chart of continuous reactor test 9

The appearance of the products was similar to the products and raw material of experiment 8. Due to this reason, the picture of these samples was not added.

Test 10: Catalyst amount increase

GC-FID results can be seen in table 16.

Table 16. GC-FID results of continuous reactor test 10

Test 10	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	8.5975	1.7225	3.79	36.2975
1	0	0.07	0	0.4525
2	8.1875	2.5075	10.325	19.605
3	11.1	4.01	16.7275	30.4
4	9.3625	4.2275	16.2875	40.4975
5	9.09	4.38	16.5775	43.0525

Figure 21 shows the GC-FID results as a line chart.

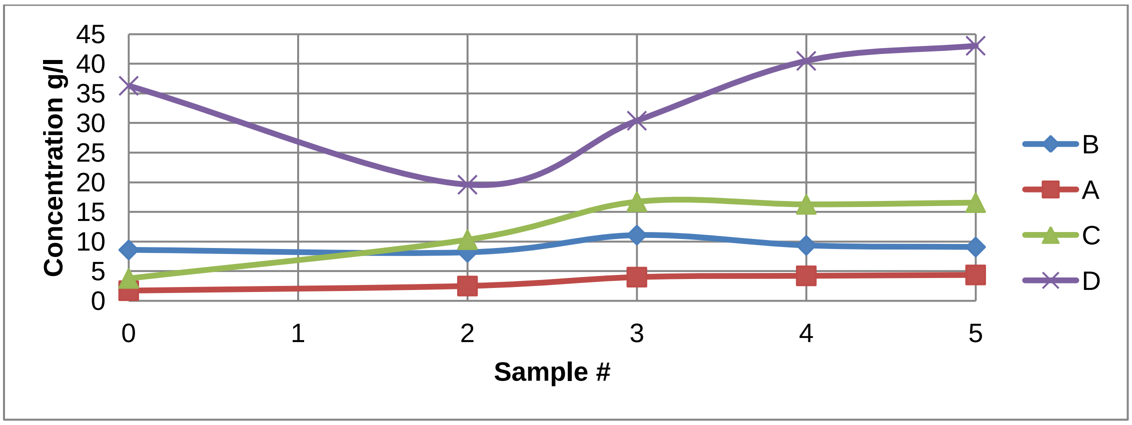

Figure 21. Line chart of continuous reactor test 10

The products had similar appearance to the products and raw material of experiment 8. Due to this reason, the picture of the samples was not added.

4.3.10 Test 11: Concentration increase

GC-FID results can be seen in table 17.

Table 17. GC-FID results of continuous reactor test 11

Test 11	**Component concentrations (g/l)**			
Sample #	**B**	**A**	**C**	**D**
0	10.615	3.2625	8.1075	68.3725
1	13.68	3.77	9.06	67.4825
2	11.16	3.5	10.97	36.9325
3	11.5175	3.925	11.7175	70.5325

Figure 22 shows the GC-FID results as a line chart.

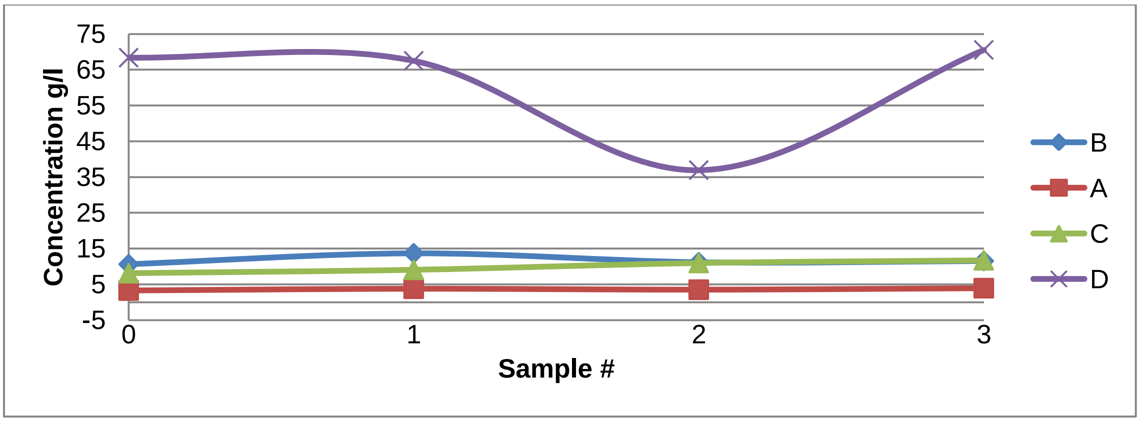

Figure 22. Line chart of continuous reactor test 10

The appearance of the products was similar to the products and raw material of experiment 8. Due to this reason, the picture of these samples was not added.

4.4 Discussion

The aim of the thesis was to do process development work on continuous C production with catalysed HDO. First three experiments were done with 15, 30 and 60 g/h raw material flow rates. The first and second sample of every test in the series represent a time when the system was unstable, meaning that it will not be taken under inspection. When comparing the colour of the products, it can be seen that they become lighter as the flow rate increases. From the GC-FID analysis results it can be seen that highest C yield is gained in 15 g/h. The analysis shows better results at lower flow rate. The component concentrations of experiments 2 and 3 are very similar to each other after the first three samples, meaning that the 60 g/h would be better choice if the process were done with high flow rates. To test if the production increases with an even slower current, the experiment 4 was conducted with a 7 g/h flow rate. The results show an increase in the C yield compared to 15 g/h, but in the experiment 1 the experimentation time was shorter. Even though the 60 g/h would produce more C per time, the 15 g/h produces better results per raw material amount. The future experiments were decided to be done using the 15 g/h flow rate. Initially it seemed as was observed with the batch reactors, that the colour of the product is a good indicator of the product quality, however the product colour of experiment 4 was lighter than in the experiment 1, which would mean that it is not the case. The C production in experiments seems to lower at the end, which could mean that the catalyst is deactivating. It was noticed that, nearly the same amount of D is produced in every test despite the different flow rates. During the process 1, the pump had accidently turned off for 9 minutes because of the pump settings, but this was estimated to have no major effect on the test results.

The test with F catalyst (reaction 5) was done with a 15 g/h flow rate to compare it to the G test results. The first two samples show high C and D production. When compared to experiment 1, these results are much higher, but the C and D production of the next samples show a gradual decline after the first two samples. The reactor weight in all experiments has been noticed to increase during the process. The experiment 5 is the only one where the reactor weight had dropped. The reason for this is most likely that the F catalyst is dissolving into X which would also explain the declining yield.

Experiment 6 was done to decrease the system stabilization time by activating the catalyst with X and hydrogen flow 1 h before start of the experiment. The first sample is most likely residue from the reactor and the second sample according to GC analysis is X, meaning they will not be taken under the study. The results after that show clearly faster stabilization of the process when compared to the unactivated experiment 1. Even though the concentrations were very similar to the experiment 1, the colour of the products was much lighter. This could mean that the observation about quality of the product is relative to the colour does not seem to apply after all.

The aim of the experiment 7 was to change the X solvent to Y. The experiment 7 had problems with pressure and temperature. These did not stay stable during the process. The results of experiment 7 were not taken under the inspection. After running the experiment with only Y to determine the best process conditions, the pressure controller was found out to be broken.

The experiments before 8 were using B synthesized before the beginning of thesis. More raw material was synthesized and it was analysed with GC-FID which showed that the material was B and suitable for the experiments. The synthesized raw material, however, was noticed to have problems. Despite being filtered with a porosity 3 glass filter, it still had a large amount of solid material in it. Due to this precipitation, the concentration of reaction mixtures could not be made accurate. The only way to estimate the true concentration is by filtering the raw material solution again and weighting the separated solid. The colour of this raw material was dark brown. This affected the colour of the products making the visual examination of the products impossible. The GC-FID analysis of the experiments 9–11 showed two peaks at retention time: 13.5 and 14 min. Initially the 14 min peak was estimated to be D product and the 13.5 min peak was possibly cis,trans C. The raw material solutions were analysed after the experiments and it was noticed that the two peaks was also seen in the raw material analysis This means that something has most likely changed with-in the raw material which is affecting the results. This was not studied further because of the thesis time limitations. Due to these reasons experiments 8–11 are not completely comparable with the earlier results, however, they still offer a usable knowledge about the process.

The experiment 8 was a retest of the experiment 7 with a fixed process controller. The first sample was mostly Y from the experiment to find the stable process conditions for Y, meaning it was not taken under the study. GC-FID results show a high D production which is likely due to the raw material problems. The amount produced C, when compared to earlier experiments are not very high. This again can be the result of the raw material or the Y solvent. The temperature of experiment 8 was set to be too high meaning that other side products could have formed. Precipitation was noticed in the catalyst bed and the raw material solution after the experiment. 0 sample was analysed after the experiment 11, meaning that it does not represent the raw material during the experiment.

The recycling system experiment 9 was done to a test batch like a flow reactor. After the first two samples, a magnetic stirrer was added to the feed/product vessel to keep the concentrations uniform. The analysis shows that D and B concentrations increase during the reaction. The C concentration begins to decrease after the second sample. This could indicate that C is reacting to either D or back to the raw material. The last sample was taken 24 h after the start of the process and it shows decreasing D concentration. This can be due to the fact that D is degrading or to some other unknown material. Due to the reactor set-up some of the X has been able to evaporate from the feed/product vessel, which can affect the results by increasing the concentration of the solution. This could also be the reason for the increasing raw material or D concentration.

In experiment 10, the amount of the catalyst was increased five times higher. The GC-FID results show a significant increase in the production. The experiment was done after the 9. Due to this, the reactor was cleaned with X feed before the experiment, meaning that the first sample is mostly X and left out from the results. The raw material was analysed after the experiment 11. Thus it does not represent the raw material during the experiment.

The purpose of the final experiment was to test the effect of doubling the concentration. Because the low amount of the raw material and short amount of project time left, the experiment lasted only 3 h. The C production seems good when compared to the earlier experiments. The number of samples was not adequate for an accurate inspection. After the experiment, it was noticed that a large amount of raw material had collected to the catalyst bed indicating that the material is not soluble enough to be used in a doubled concentration. This problem of precipitation was also noticed during preparing the raw material solution. From the catalyst bed it was also noticed that the hardening, due to raw material collection, could only be seen on one side of the catalyst bed, which could indicate that the raw material is not flowing through the whole catalyst bed.

An unknown peak could be seen in some of the continuous GC-FID results near at 6.5 min. The samples, which had this peak, were analysed with GC-MS. The peak was discovered to be L.

5 Conclusions

From batch reactor experiments, it is clear that reactor ii with a proper lagging is the only working reactor. The other reactors seem to be too contaminated for sensitive reagents like precious metal catalysts. The reactor 4 even with a new Teflon cup did not produce good results compared to reactor ii.

If the project time allowed to accurately determine the causes of the batch reactor problems, then more experiments should be conducted with pressure reactors. The Reactor ii should be retested. This would confirm the repeatability of the reaction. The reactor iv with a new Teflon cup should be done to verify the reaction problems with nylon. The unknown pressure rise of reactor ii should be investigated further which could provide interesting knowledge about why the reactor ii produced such significant results.

The continuous reactor experiments produced good results. The low flow rates seem to be the best for the reaction due to preferable reaction mixture composition. However, 60 g/h flow rate produces more C faster than 15 g/h. The G is more viable for continuous reactor process than F, due to the solubility and cost of F. The Y solvent has production problems, but further studies should be conducted using it, as it is bio derivable and more affordable than X.

The continuous reactor experiments indicate that results seem to decline at the end of reaction thus the robustness of the G catalyst should be studied with longer experimentation time. Y experiment should be repeated, because of the problems with the raw material. The results of catalyst increase are significant. Even though the experiment was conducted using the problematic starting material, there is no need to repeat the experiment. The future tests should use the same amounts of the catalyst bed chemicals. The increased catalyst and inert or more increased inert material tests should be experimented with a 60 g/h flow rate, which could give a high production rate. The raw material is not soluble enough for concentration increase. The possibility that the material is not going through the whole catalyst bed would be a significant fact to confirm.

Initially it seemed that the colour of product was a good indicator of the product quality, when batch reactor experiments were observed. However the continuous reactor experiment results to seem show that this is not the case. The source of colour in experiment 1 products is unknown and should be researched.

Other reactor possibilities should also be considered. A slurry reactor, for example, can be used in gas-liquid-solid reactions in which the solid catalyst is mixed in with a liquid. The gas is introduced to the system by bubbling it from the bottom of the reactor. In the slurry reactor process, the catalyst is more in touch with the liquid potentially causing a higher reaction rate. Slurry reactors also offer a better temperature control. The problem with the slurry reactor would be the need for separation unit to remove the catalyst from the solution. [27, p.375; 28, p. 210]

The project did not allow enough time for the process optimization. To search for the best possible process optimum, using Design of Experiments (DOE) design would be recommended. DOE can reveal which factors are significant or how the factors affect each other. It can used to produce a model for the process, which can be used to search the optimum maximum. Firstly the quantity of process factors is determined. High and low values for the factors used in tests are decided and these are coded into 1 and -1. The number of tests can be determined using 2^n-method, where n is the number of test factors. Then the tests are then planned by creating a table with all of the possible factor combinations. These experiments should be conducted in a random order to ensure a statistical independence of the results. When the experiments are complete, the data can be processed to create the process model and response surface with, for example, excel or design of experiments specific software. The response surface can be used to look for a local or best possible optimum. A couple of zero point experiments, in which the tests are conducted at midpoints of the facto values, should also be included in the test design. If the subtraction of the average of zero points and test results differs from the test error, this could signify that the process model is nonlinear. If the process model is nonlinear more experiments have to be conducted. The nonlinear model can be produced by using Central Composite Design, in which experiments are conducted with all factors except one as zero. This is done to every value. An example for DOE design with CC can be seen in table 18. [29]

Table 18. DOE example with CC

2^n-method			
Test number	**Temperature**	**Pressure**	**Feed rate**
1	1	1	1
2	-1	-1	-1
3	1	-1	-1
4	-1	1	-1
5	-1	-1	1
6	-1	1	1
7	1	-1	1
8	1	1	-1
9	0	0	0
10	0	0	0
11	0	0	0
CC-design			
Test number	**Temperature**	**Pressure**	**Feed rate**
12	1	0	0
13	0	1	0
14	0	0	1
15	-1	0	0
16	0	-1	0
17	0	0	-1

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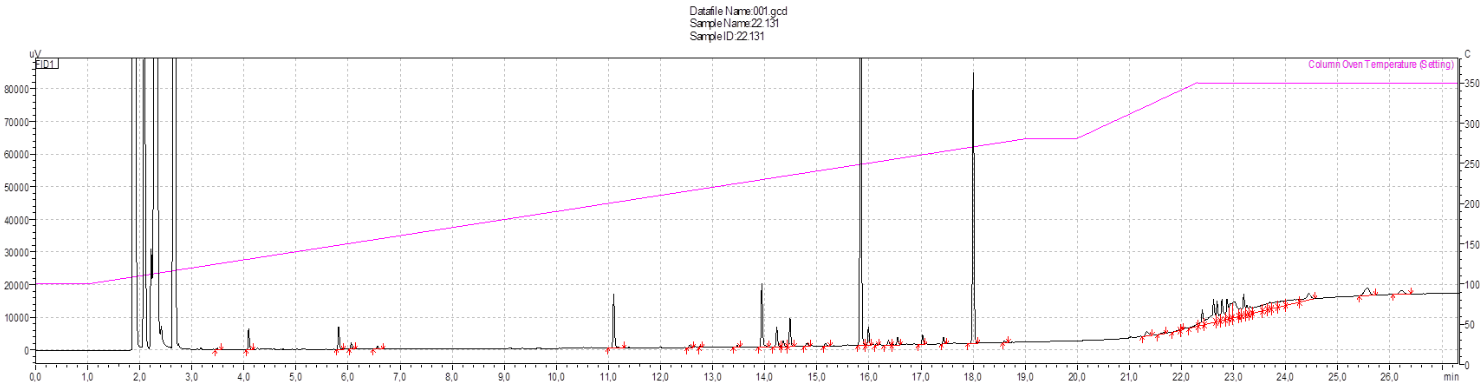
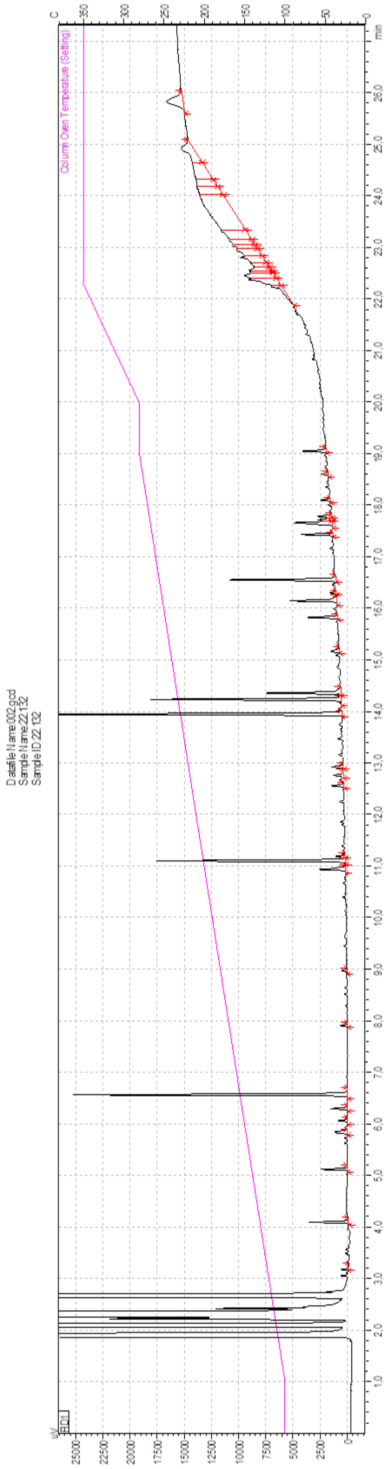
Reactor i GC-FID



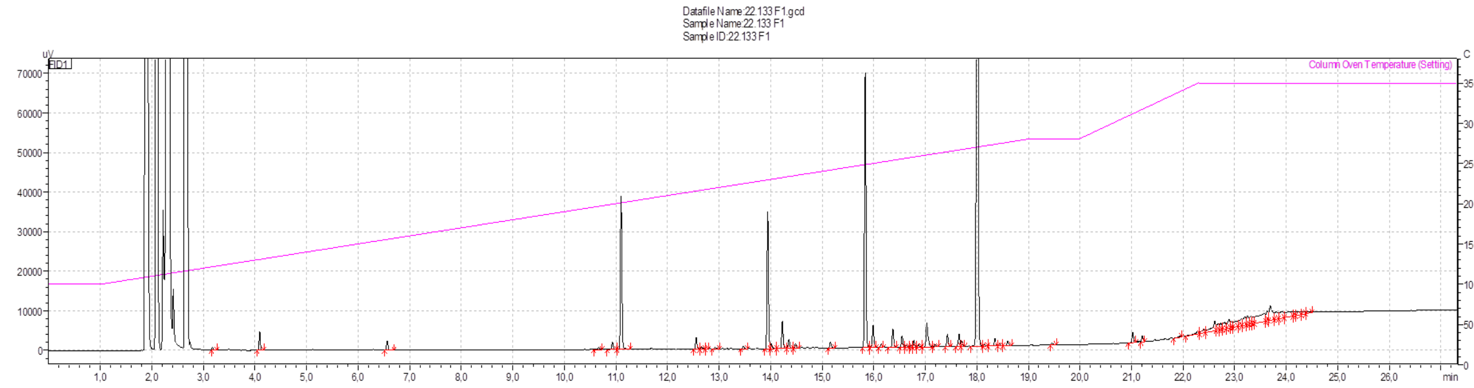
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.97	g/l	22, 23, 24	166750	84871	18.176
2	A	16.024	2.043	g/l	16, 17, 18, 19, 20	278460	142828	30.353
3	C	11.1	0.771	g/l	6	33786	16355	3.683
4	D	13.887	2.106	g/l	9, 10, 11, 12, 13	73315	36143	7.991

Reactor ii GC-FID



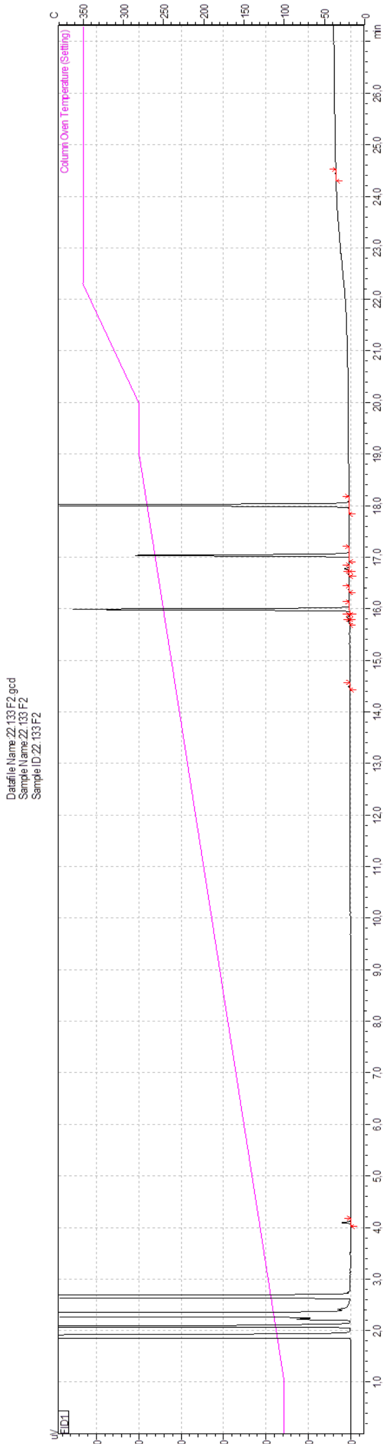
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.293	g/l	24, 25, 26, 27, 28, ...	24840	10508	3.983
2	A	16.024	0.27	g/l	20, 21, 22, 23	36872	17304	5.913
3	C	11.156	0.961	g/l	10, 11, 12	42117	20524	6.754
4	D	13.887	3.356	g/l	16, 17, 18	116823	56912	18.734

Reactor iv fraction 1 GC-FID



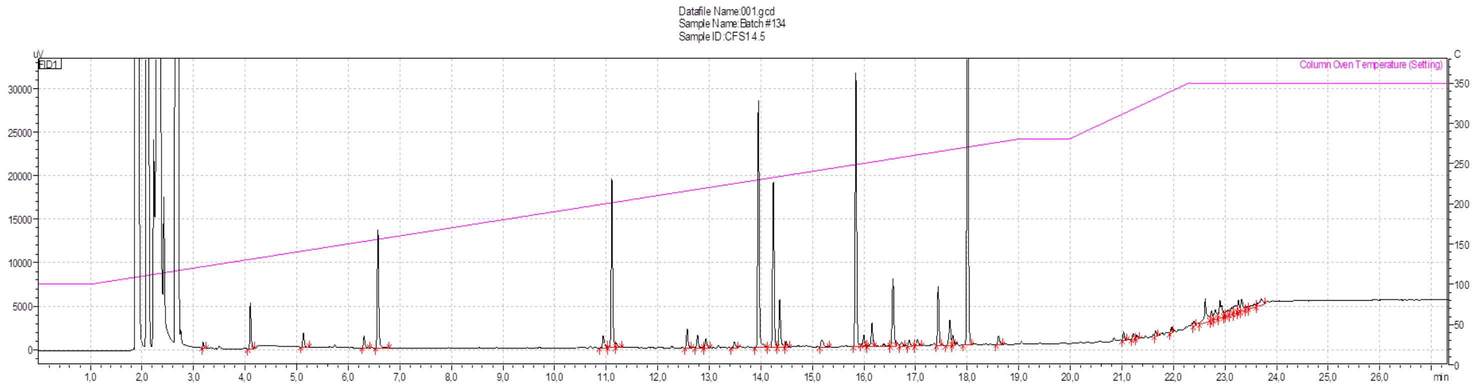
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	6.272	g/l	28, 29, 30, 31, 32, ...	530930	266129	47.789
2	A	16.024	1.248	g/l	18, 19, 20, 21, 22, ...	170117	84799	15.312
3	C	11.156	1.833	g/l	4, 5, 6	80349	40733	7.232
4	D	13.887	2.691	g/l	11, 12, 13, 14, 15, ...	93676	46514	8.432

Reactor iv fraction 2 GC-FID



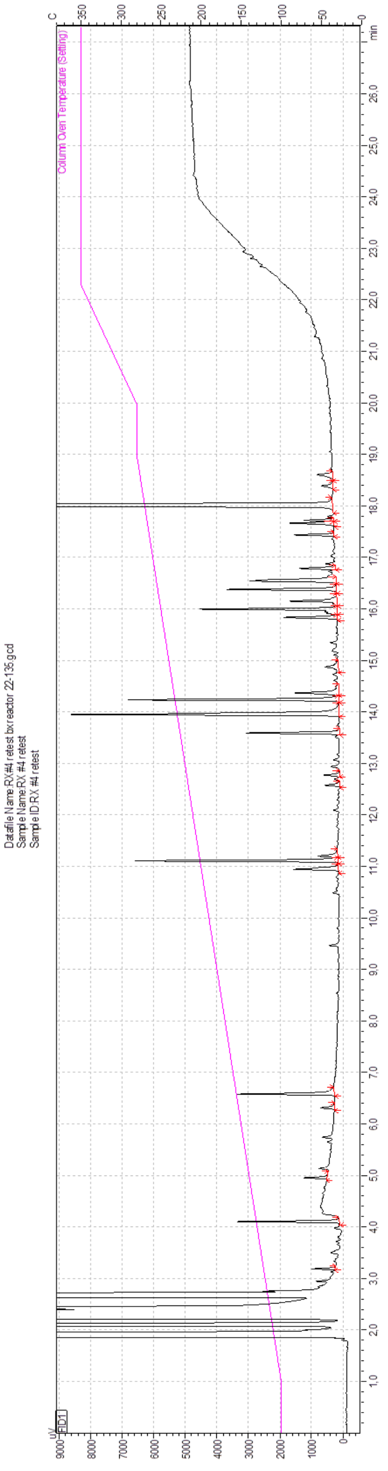
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.008	6.481	g/l	10	548659	262836	47.77
2	A	16.024	2.479	g/l	3, 4, 5, 6, 7, ...	337947	169029	29.424
3	C	No peak is detected.	0	g/l	--	0	0	0
4	D	14.483	0.05	g/l	2	1743	873	0.152

Reactor ii Retest GC-FID



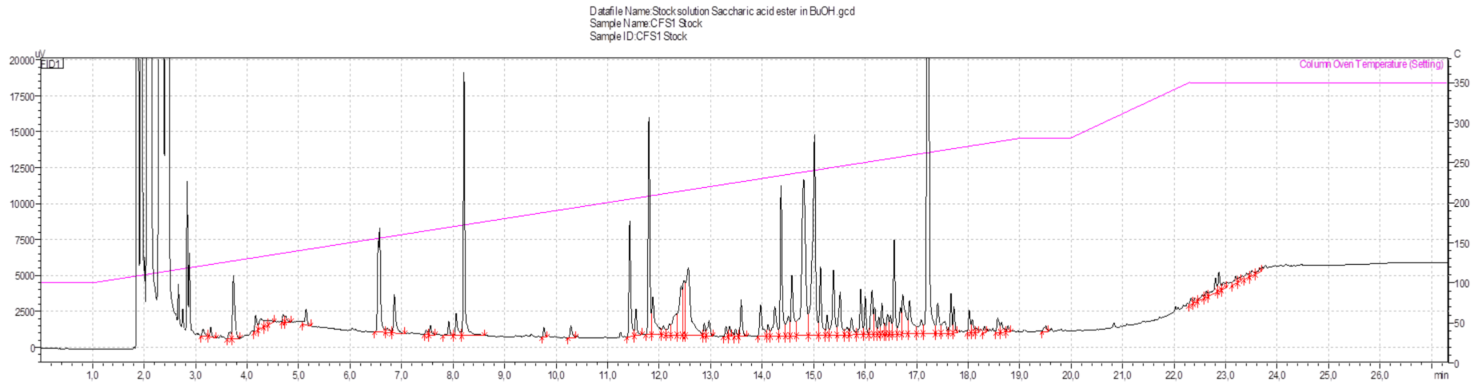
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.548	g/l	25, 26, 27, 28, 29	131002	67713	26.277
2	A	16.024	0.681	g/l	18, 19, 20, 21, 22	92813	43297	18.617
3	C	11.156	1.002	g/l	6, 7, 8	43918	21206	8.809
4	D	13.887	3.232	g/l	12, 13, 14, 15, 16	112526	53860	22.571

Reactor iv Retest GC-FID



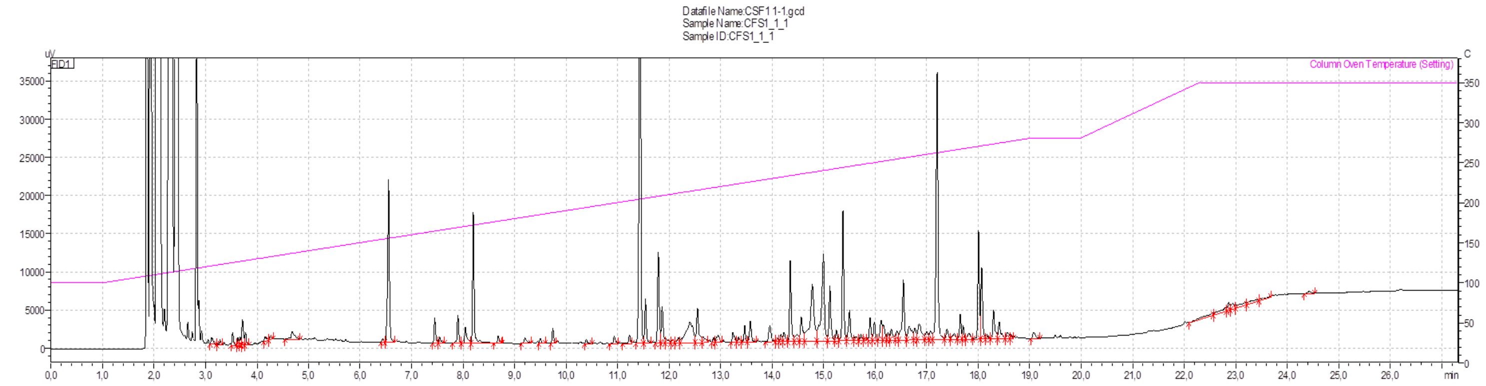
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.105	g/l	22, 23, 24, 25, 26, ...	347526	173936	73.615
2	A	16.024	0.269	g/l	16, 17, 18, 19, 20, ...	36707	14828	7.775
3	C	11.156	0.433	g/l	6, 7, 8	18988	8371	4.022
4	D	13.887	1.391	g/l	11, 12, 13, 14	48429	19301	10.259

Continuous experiment 1–6: Raw material



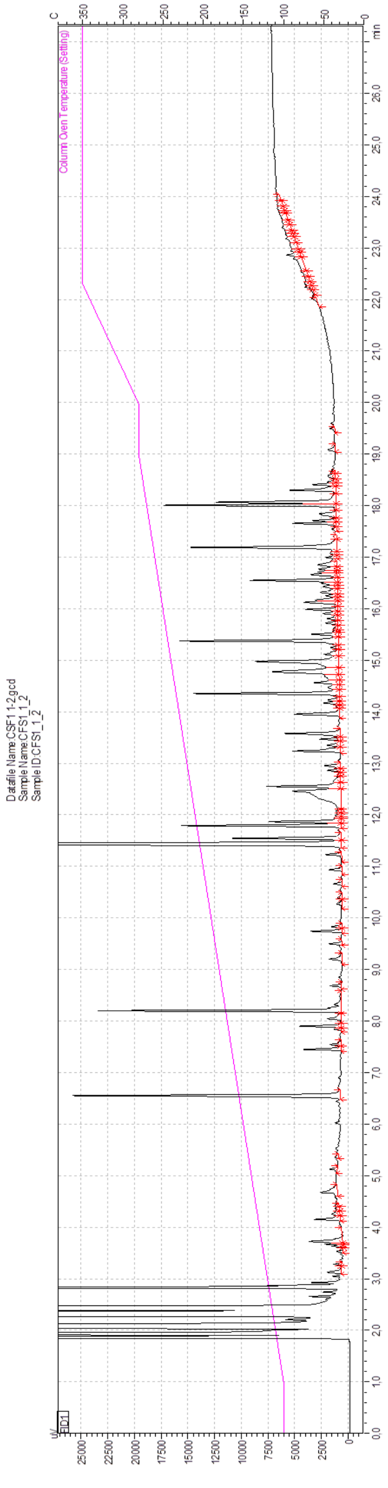
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.151	g/l	66, 67, 68, 69, 70, ...	182071	65529	22.248
2	A	16.024	0.846	g/l	47, 48, 49, 50, 51, ...	115342	39169	14.094
3	C	11.156	0.548	g/l	22, 23	24036	9880	2.937
4	D	13.887	2.239	g/l	34, 35, 36, 37, 38, ...	77951	25478	9.525
5	E	7.18	0.303	g/l	14, 15	9206	3005	1.125

Continuous experiment 1: Sample 1



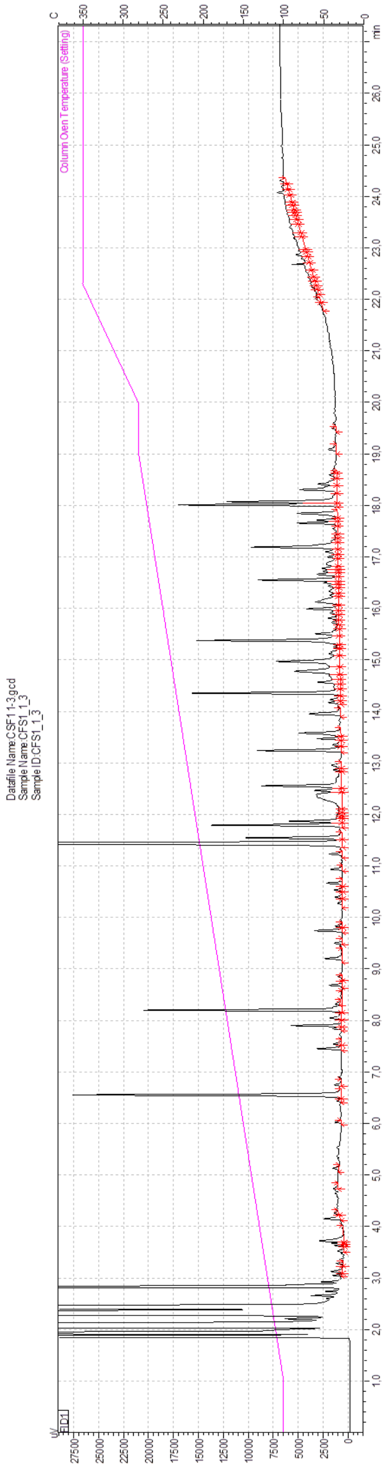
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.247	g/l	70, 71, 72, 73, 74, ...	190231	74282	19.805
2	A	16.024	1	g/l	51, 52, 53, 54, 55, ...	136343	49145	14.194
3	C	11.156	3.568	g/l	23, 24, 25, 26	156376	64457	16.28
4	D	13.887	2.062	g/l	37, 38, 39, 40, 41, ...	71774	26092	7.472

Continuous experiment 1: Sample 2



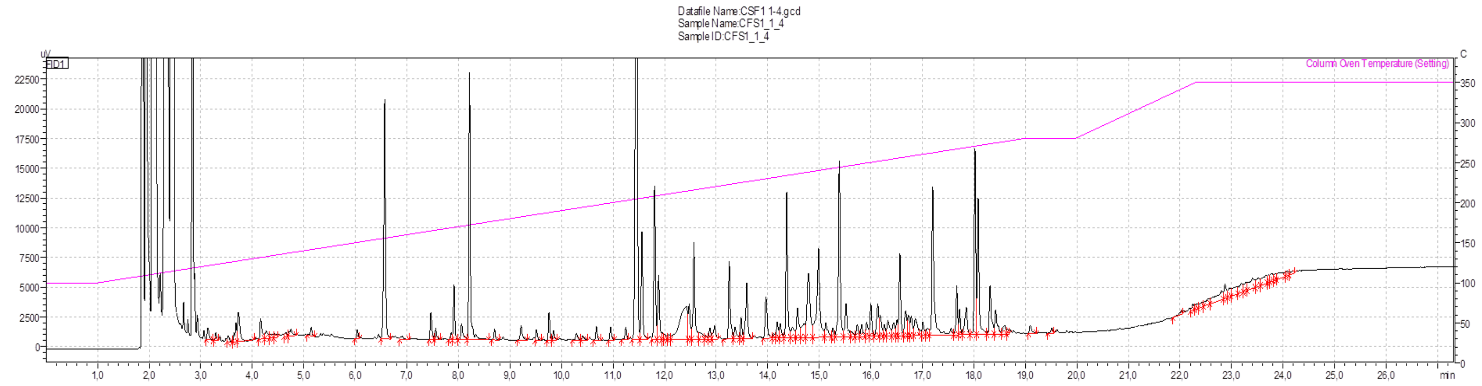
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.723	g/l	81, 82, 83, 84, 85, ...	145829	57935	13.674
2	A	16.024	0.972	g/l	59, 60, 61, 62, 63, ...	132514	50599	12.426
3	C	11.156	4.927	g/l	28, 29, 30, 31, 32	215951	87960	20.25
4	D	13.887	2.807	g/l	44, 45, 46, 47, 48, ...	97727	36514	9.164

Continuous experiment 1: Sample 3



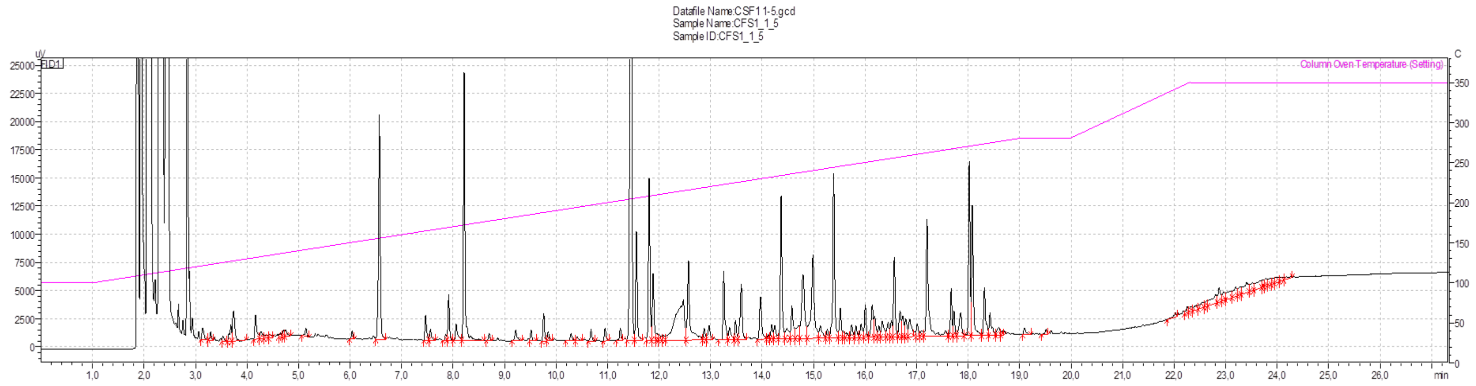
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.684	g/l	81, 82, 83, 84, 85, ...	142522	53767	13.964
2	A	16.024	0.922	g/l	61, 62, 63, 64, 65, ...	125703	43552	12.316
3	C	11.156	4.551	g/l	32, 33, 34, 35, 36	199470	84288	19.544
4	D	13.887	2.801	g/l	47, 48, 49, 50, 51, ...	97511	38665	9.554

Continuous experiment 1: Sample 4



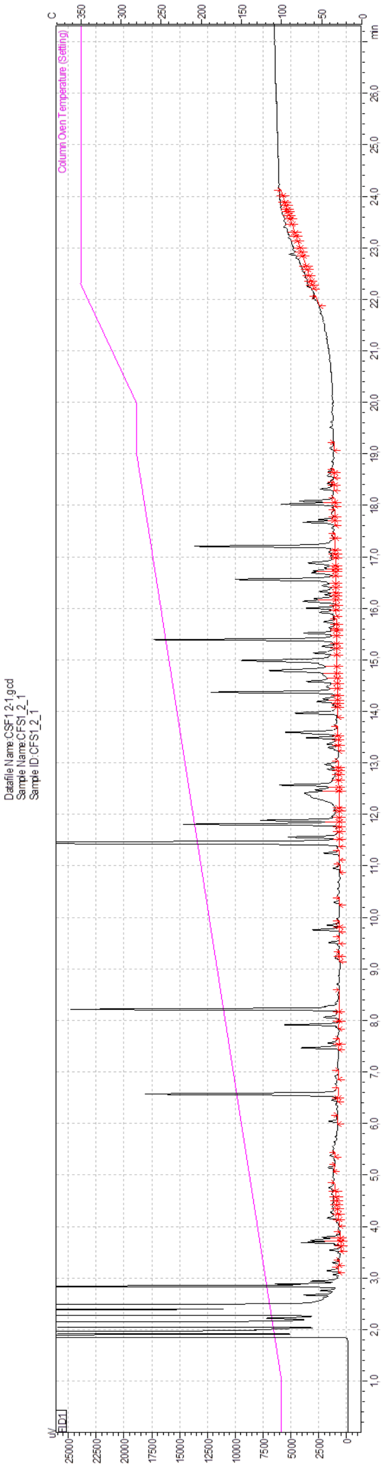
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.682	g/l	82, 83, 84, 85, 86, ...	142373	54918	14.611
2	A	16.024	0.909	g/l	61, 62, 63, 64, 65, ...	123893	45855	12.715
3	C	11.156	4.254	g/l	29, 30, 31, 32, 33	186427	78580	19.133
4	D	13.887	2.692	g/l	46, 47, 48, 49, 50, ...	93724	35595	9.619

Continuous experiment 1: Sample 5



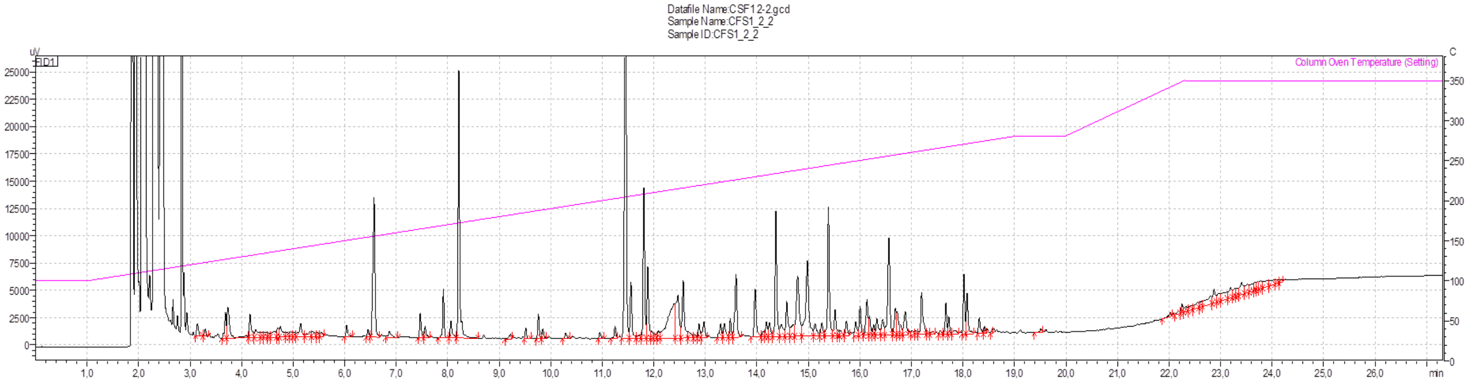
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.606	g/l	80, 81, 82, 83, 84, ...	135970	52742	13.838
2	A	16.024	0.929	g/l	58, 59, 60, 61, 62, ...	126670	47669	12.892
3	C	11.156	4.191	g/l	29, 30, 31, 32, 33	183666	77613	18.692
4	D	13.887	2.802	g/l	43, 44, 45, 46, 47, ...	97564	36580	9.929

Continuous experiment 2: Sample 1



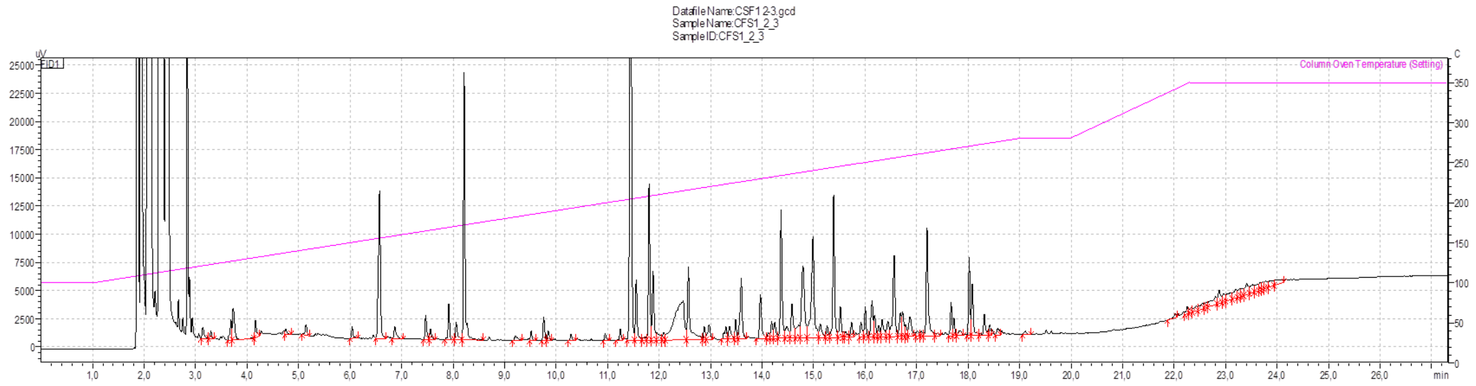
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.866	g/l	83, 84, 85, 86, 87, ...	73308	28715	8.136
2	A	16.024	0.971	g/l	63, 64, 65, 66, 67, ...	132319	49862	14.686
3	C	11.156	3.661	g/l	32, 33, 34, 35, 36	160448	66464	17.807
4	D	13.887	2.566	g/l	48, 49, 50, 51, 52, ...	89348	32007	9.916

Continuous experiment 2: Sample 2



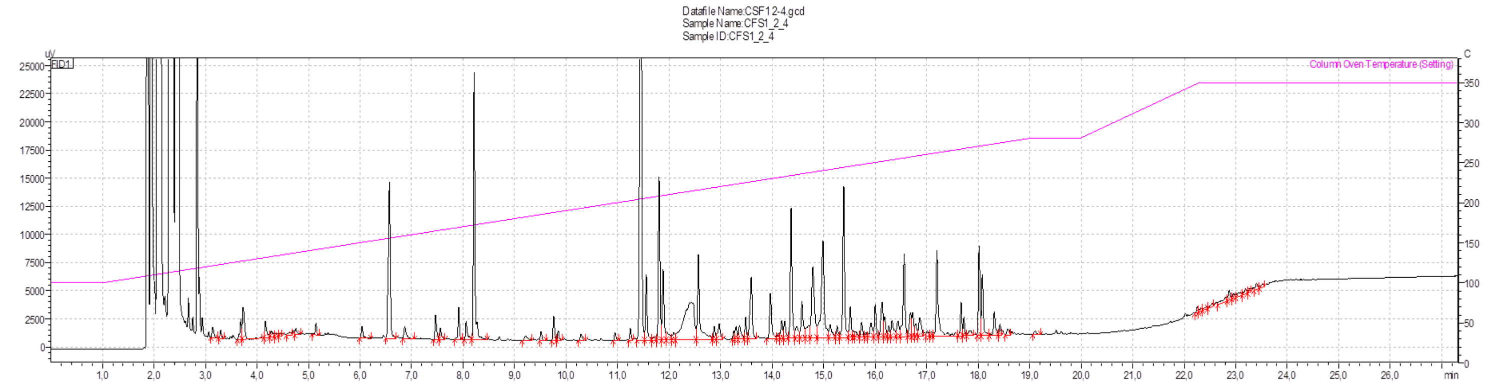
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.633	g/l	87, 88, 89, 90, 91, ...	53596	21237	6.234
2	A	16.024	0.891	g/l	67, 68, 69, 70, 71, ...	121516	44735	14.133
3	C	11.156	2.979	g/l	35, 36, 37, 38, 39	130553	57061	15.184
4	D	13.887	2.611	g/l	52, 53, 54, 55, 56, ...	90887	33139	10.571

Continuous experiment 2: Sample 3



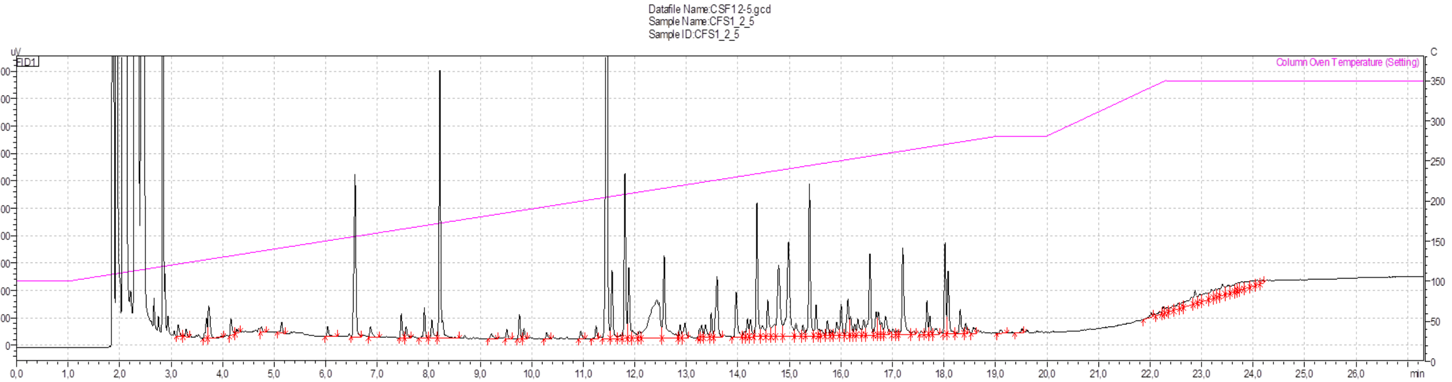
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.89	g/l	69, 70, 71, 72, 73, ...	75319	29624	9.005
2	A	16.024	0.865	g/l	49, 50, 51, 52, 53, ...	117954	44140	14.102
3	C	11.156	3.113	g/l	21, 22, 23, 24, 25	136443	57799	16.312
4	D	13.887	2.553	g/l	34, 35, 36, 37, 38, ...	88869	31954	10.625

Continuous experiment 2: Sample 4



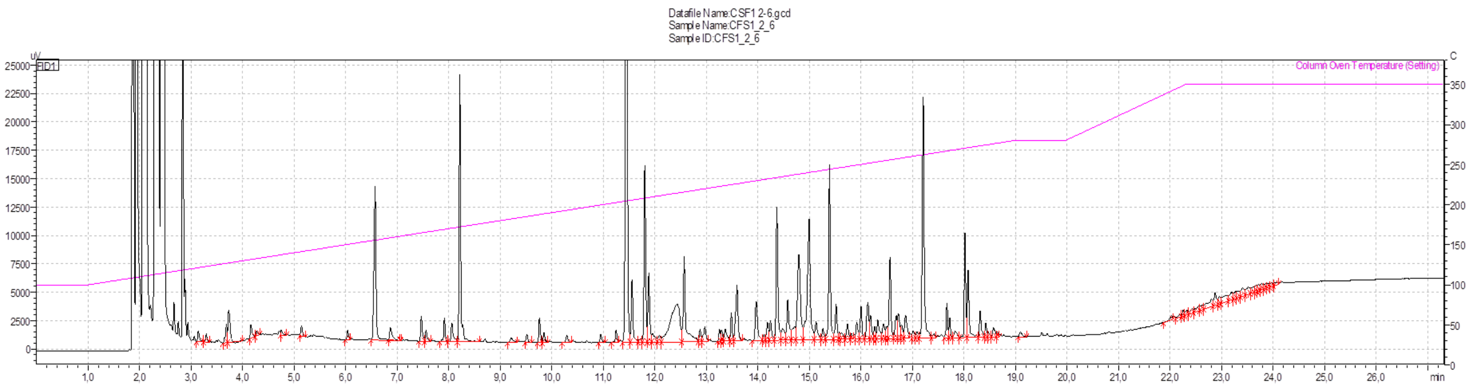
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.891	g/l	75, 76, 77, 78, 79, ...	75431	29368	9.191
2	A	16.024	0.894	g/l	54, 55, 56, 57, 58, ...	121833	45494	14.845
3	C	11.156	3.337	g/l	25, 26, 27, 28, 29	146247	61471	17.819
4	D	13.887	2.649	g/l	38, 39, 40, 41, 42, ...	92228	33754	11.237

Continuous experiment 2: Sample 5



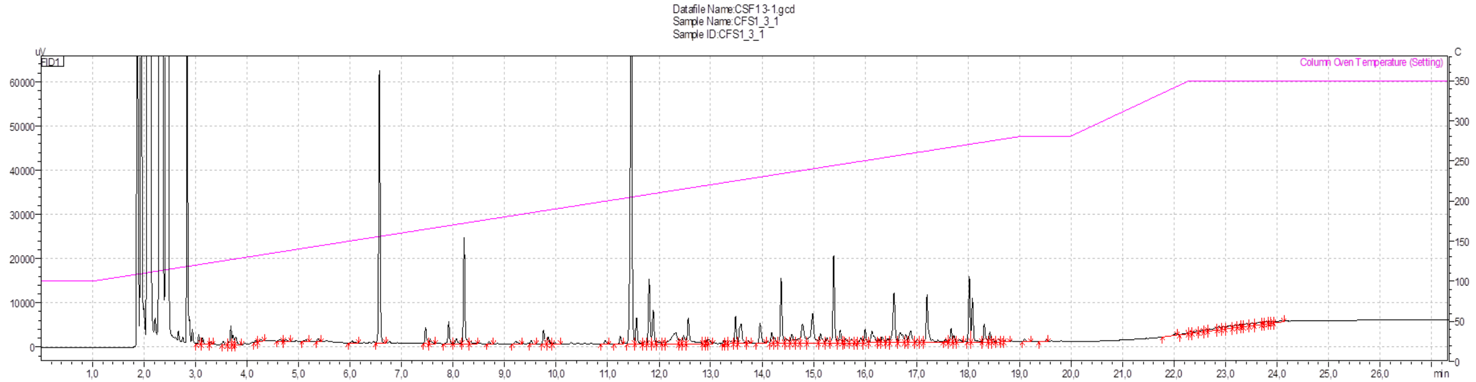
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.951	g/l	72, 73, 74, 75, 76, ...	80545	31589	8.966
2	A	16.024	0.908	g/l	51, 52, 53, 54, 55, ...	123835	46247	13.785
3	C	11.156	3.531	g/l	22, 23, 24, 25, 26	154728	64948	17.224
4	D	13.887	2.738	g/l	35, 36, 37, 38, 39, ...	95327	35055	10.611

Continuous experiment 2: Sample 6



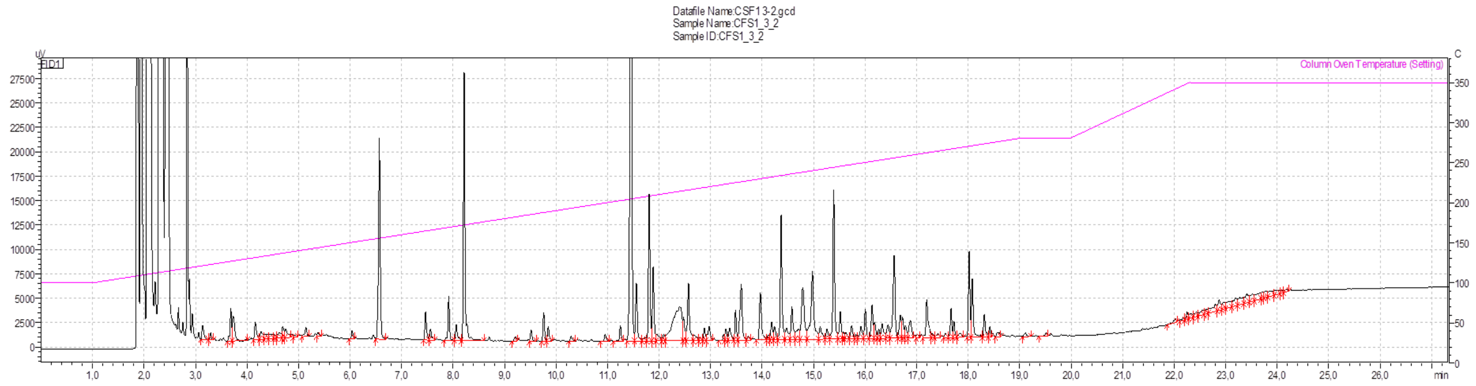
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.375	g/l	73, 74, 75, 76, 77, ...	116402	47148	12.655
2	A	16.024	0.947	g/l	51, 52, 53, 54, 55, ...	129046	49681	14.03
3	C	11.156	3.494	g/l	22, 23, 24, 25, 26	153122	63256	16.647
4	D	13.887	2.682	g/l	35, 36, 37, 38, 39, ...	93373	33669	10.151

Continuous experiment 3: Sample 1



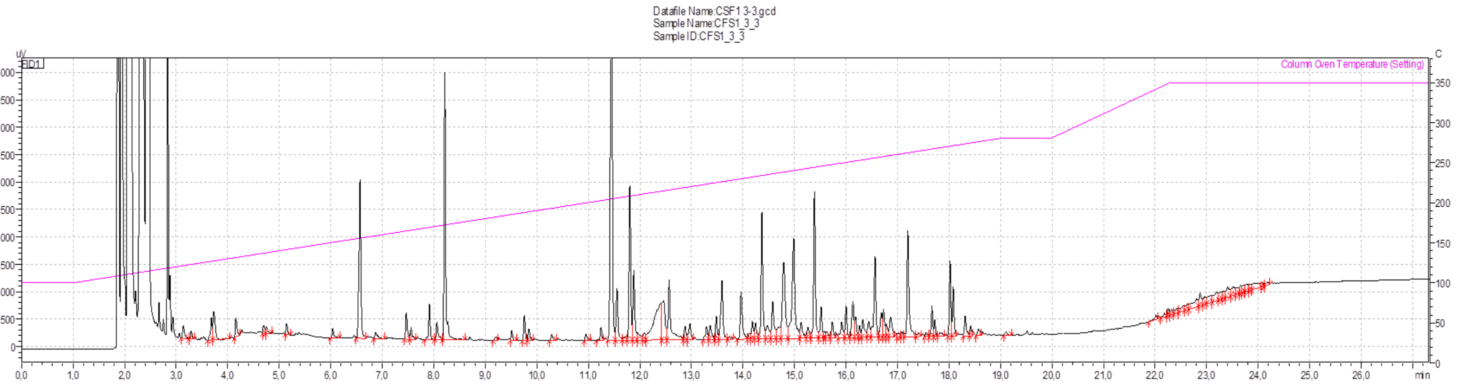
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.41	g/l	79, 80, 81, 82, 83, ...	119337	49038	11.07
2	A	16.024	1.074	g/l	60, 61, 62, 63, 64, ...	146396	52016	13.58
3	C	11.156	5.207	g/l	28, 29, 30, 31, 32	228214	90465	21.169
4	D	13.887	2.988	g/l	44, 45, 46, 47, 48, ...	104008	39257	9.648

Continuous experiment 3: Sample 2



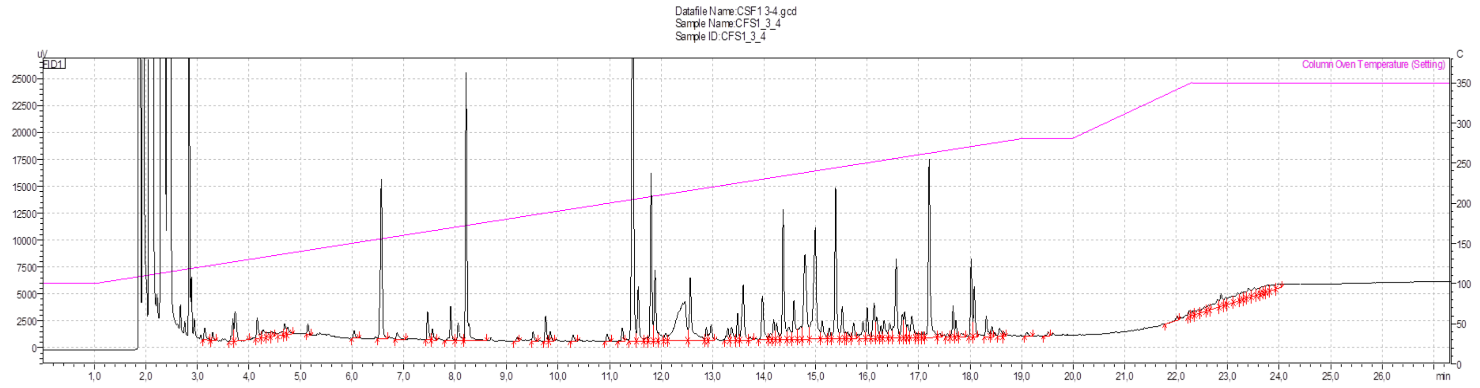
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.858	g/l	81, 82, 83, 84, 85, ...	72660	28703	7.617
2	A	16.024	0.975	g/l	61, 62, 63, 64, 65, ...	132982	49606	13.94
3	C	11.156	4.068	g/l	28, 29, 30, 31, 32	178269	74847	18.687
4	D	13.887	2.98	g/l	44, 45, 46, 47, 48, ...	103758	37747	10.877

Continuous experiment 3: Sample 3



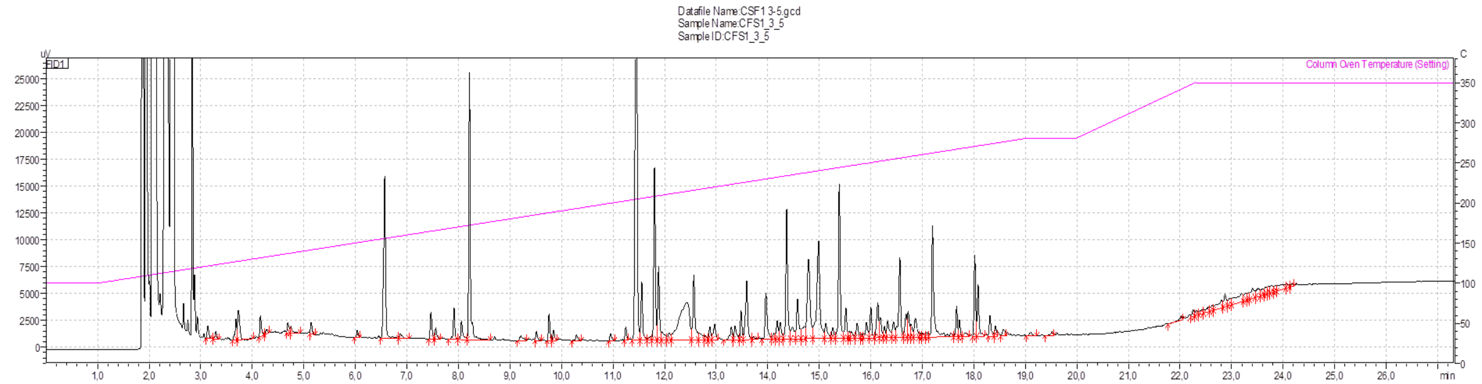
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.863	g/l	72, 73, 74, 75, 76, ...	73097	29443	8.425
2	A	16.024	0.914	g/l	52, 53, 54, 55, 56, ...	124615	46627	14.364
3	C	11.156	3.161	g/l	22, 23, 24, 25, 26	138523	59675	15.967
4	D	13.887	2.784	g/l	36, 37, 38, 39, 40, ...	96921	34072	11.171

Continuous experiment 3: Sample 4



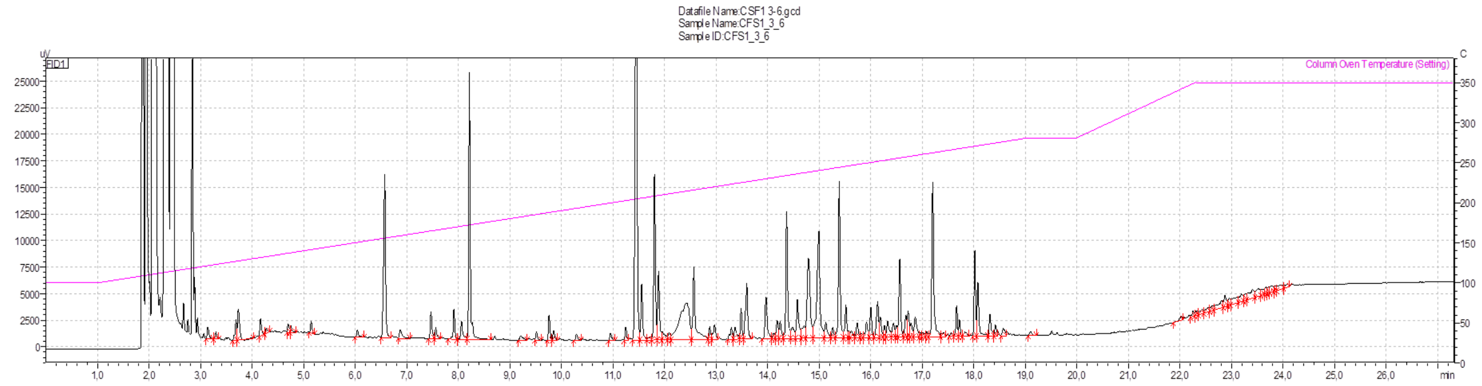
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.108	g/l	76, 77, 78, 79, 80, …	93760	37741	10.108
2	A	16.024	0.955	g/l	55, 56, 57, 58, 59, …	130158	47616	14.031
3	C	11.156	3.36	g/l	26, 27, 28, 29, 30	147266	61872	15.876
4	D	13.887	2.847	g/l	39, 40, 41, 42, 43, …	99123	34751	10.686

Continuous experiment 3: Sample 5



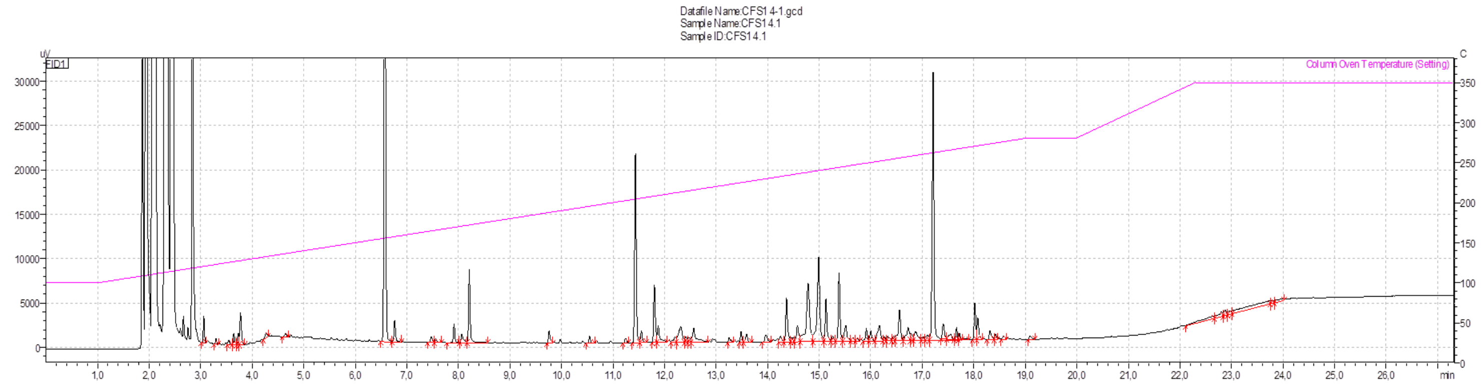
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.938	g/l	76, 77, 78, 79, 80, ...	79371	30949	8.682
2	A	16.024	0.956	g/l	54, 55, 56, 57, 58, ...	130331	48010	14.256
3	C	11.156	3.483	g/l	23, 24, 25, 26, 27	152651	63293	16.697
4	D	13.887	2.905	g/l	38, 39, 40, 41, 42, ...	101136	35687	11.062

Continuous experiment 3: Sample 6



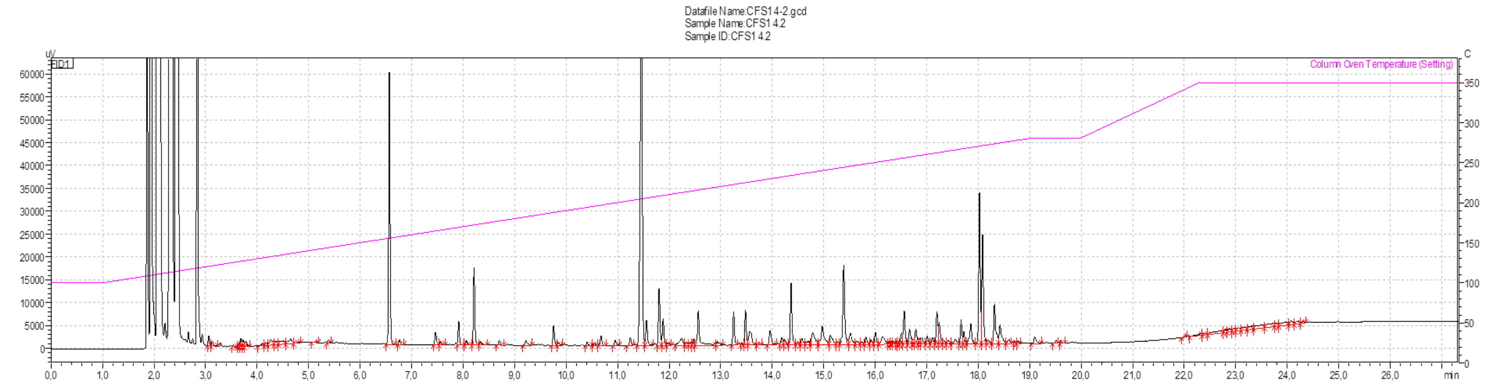
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.091	g/l	74, 75, 76, 77, 78, ...	92349	36844	10.052
2	A	16.024	0.955	g/l	51, 52, 53, 54, 55, ...	130222	49460	14.174
3	C	11.156	3.516	g/l	23, 24, 25, 26, 27	154105	65049	16.774
4	D	13.887	2.802	g/l	36, 37, 38, 39, 40, ...	97552	34436	10.618

Continuous experiment 4: Sample 1



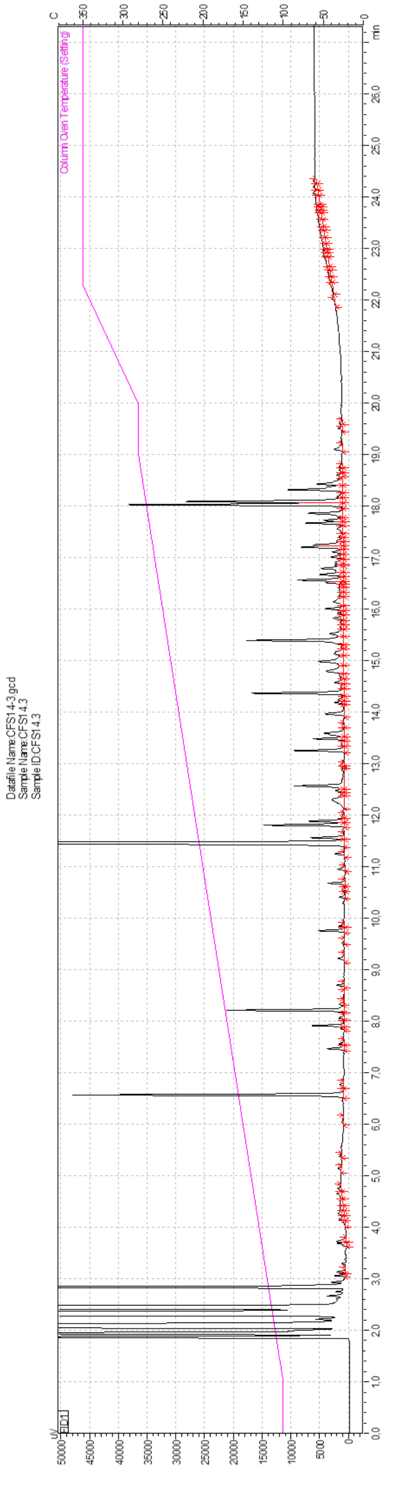
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.287	g/l	56, 57, 58, 59, 60, ...	108927	42549	15.523
2	A	16.024	0.493	g/l	39, 40, 41, 42, 43, ...	67162	22182	9.571
3	C	11.156	1.151	g/l	18, 19, 20	50430	22866	7.187
4	D	13.887	0.94	g/l	28, 29, 30, 31, 32, ...	32725	11486	4.664

Continuous experiment 4: Sample 2



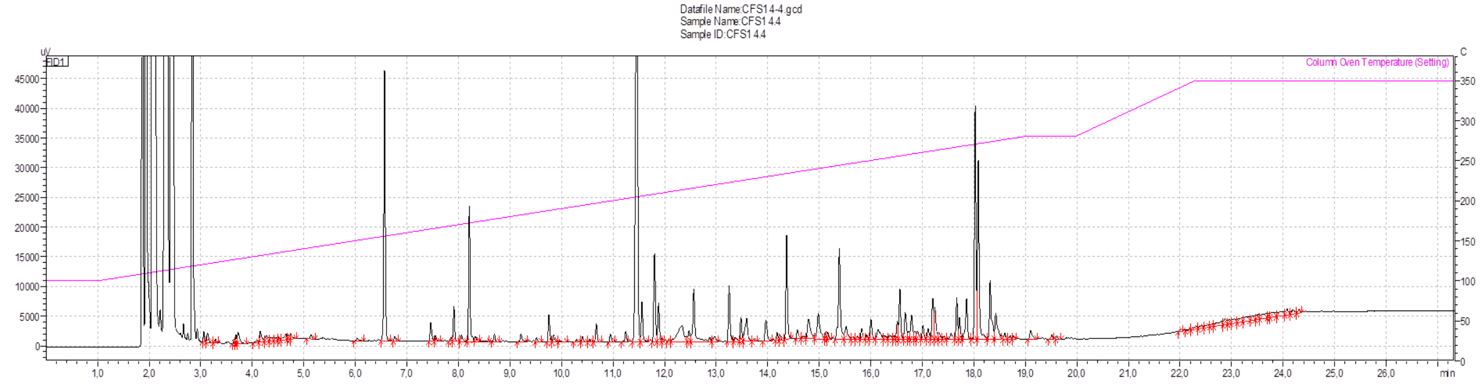
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.854	g/l	82, 83, 84, 85, 86, ...	241640	99986	20.065
2	A	16.024	0.995	g/l	60, 61, 62, 63, 64, ...	135700	48785	11.268
3	C	11.156	6.114	g/l	31, 32, 33, 34, 35	267961	101656	22.251
4	D	13.887	2.873	g/l	45, 46, 47, 48, 49, ...	100003	39709	8.304

Continuous experiment 4: Sample 3



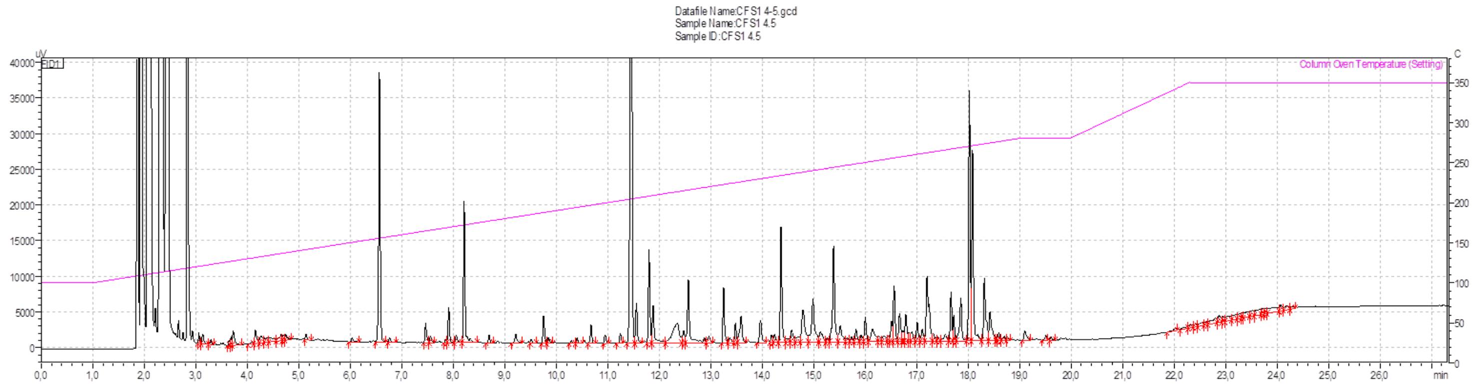
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.325	g/l	79, 80, 81, 82, 83, ...	281457	114498	22.117
2	A	16.024	1.093	g/l	60, 61, 62, 63, 64, ...	148972	50054	11.706
3	C	11.156	6.06	g/l	31, 32, 33, 34, 35	265577	104230	20.869
4	D	13.887	3.121	g/l	45, 46, 47, 48, 49, ...	108644	42544	8.537

Continuous experiment 4: Sample 4



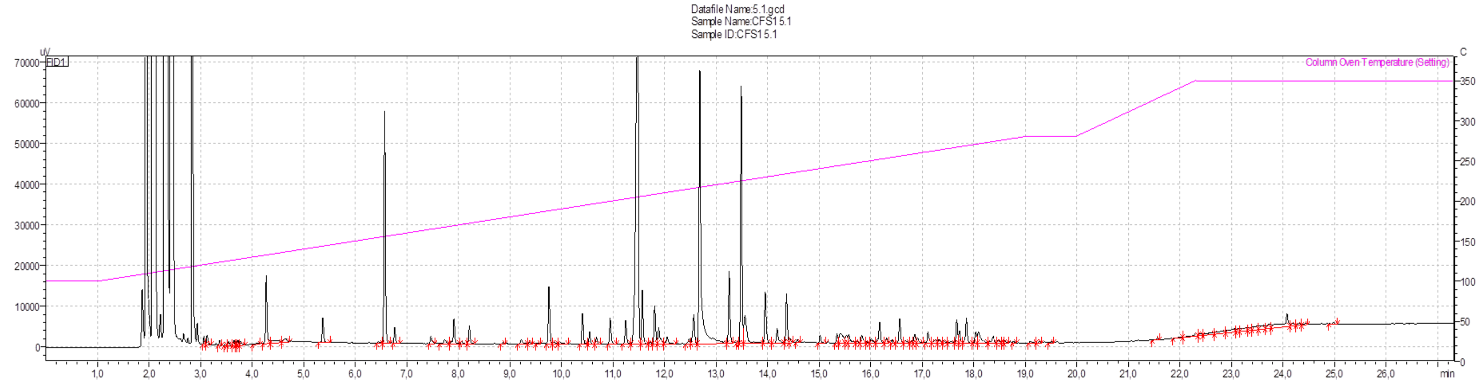
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.401	g/l	83, 84, 85, 86, 87, ...	287866	119566	22.378
2	A	16.024	1	g/l	64, 65, 66, 67, 68, ...	136352	48960	10.6
3	C	11.156	6.117	g/l	36, 37, 38, 39, 40	268091	102732	20.841
4	D	13.887	2.973	g/l	49, 50, 51, 52, 53, ...	103496	42997	8.046

Continuous experiment 4: Sample 5



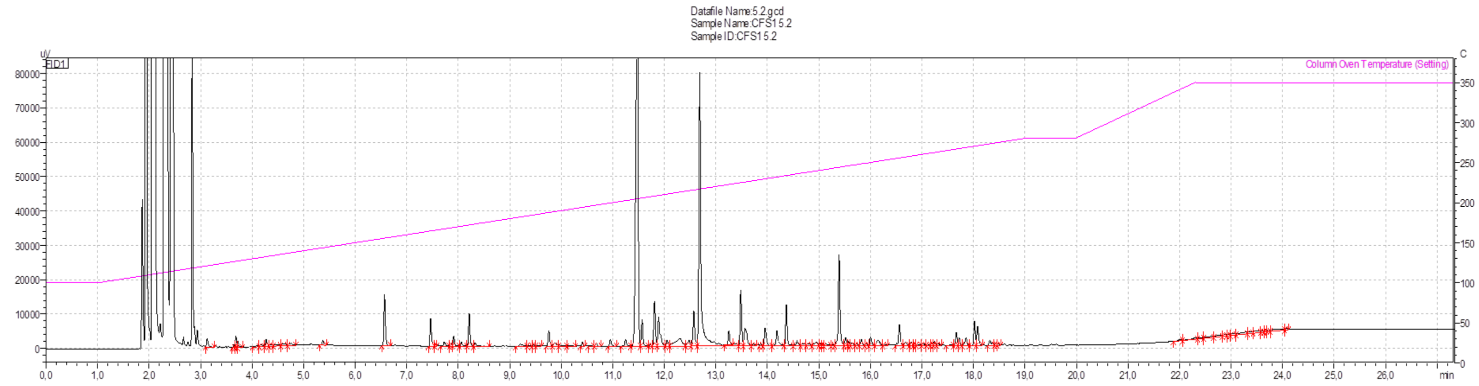
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.241	g/l	77, 78, 79, 80, 81, ...	274336	106750	22.766
2	A	16.024	1.03	g/l	57, 58, 59, 60, 61, ...	140460	47819	11.656
3	C	11.156	5.106	g/l	32, 33, 34, 35, 36	223760	89235	18.569
4	D	13.887	2.821	g/l	43, 44, 45, 46, 47, ...	98203	38766	8.149

Continuous experiment 5: Sample 1



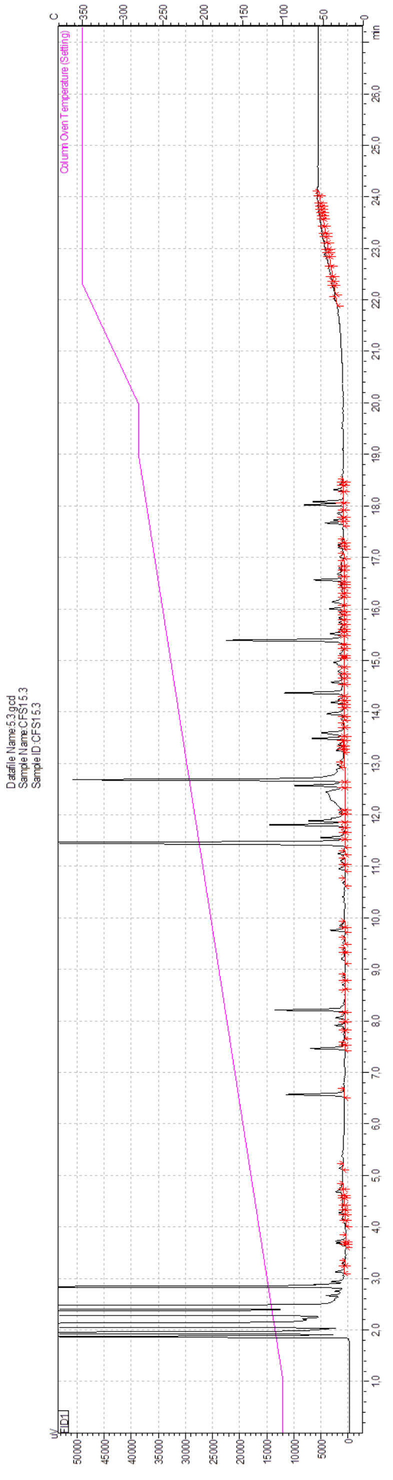
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.008	g/l	70, 71, 72, 73, 74, ...	85335	29995	5.75
2	A	16.024	0.622	g/l	54, 55, 56, 57, 58, ...	84768	27623	5.711
3	C	11.156	9.321	g/l	32, 33, 34, 35, 36, ...	408507	143408	27.523
4	D	13.887	7.382	g/l	44, 45, 46, 47, 48, ...	256992	116539	17.315

Continuous experiment 5: Sample 2



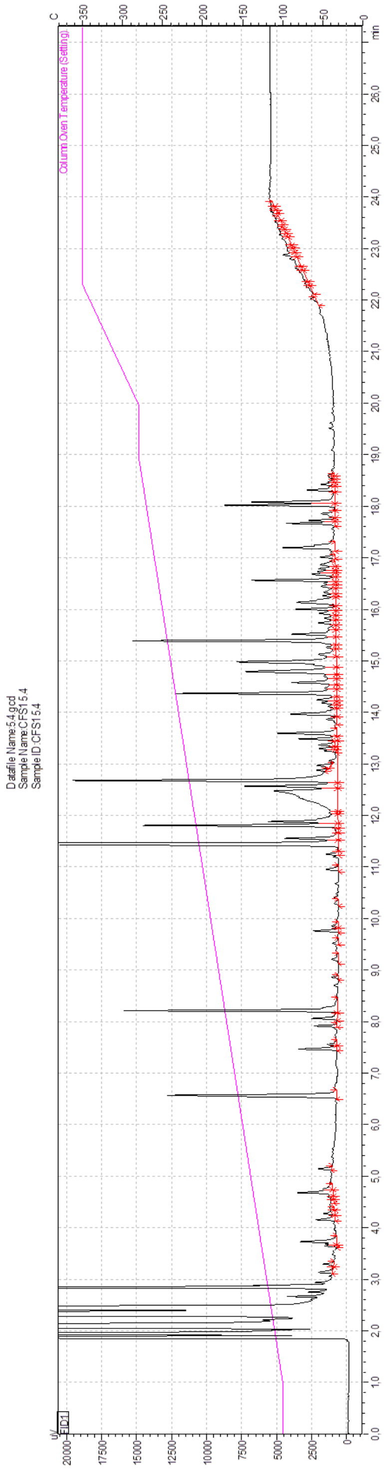
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.777	g/l	77, 78, 79, 80, 81, ...	65789	26766	5.206
2	A	16.024	0.887	g/l	60, 61, 62, 63, 64, ...	120885	46582	9.566
3	C	11.156	8.701	g/l	32, 33, 34, 35, 36, ...	381309	132601	30.176
4	D	13.887	3.64	g/l	45, 46, 47, 48, 49, ...	126724	49187	10.029

Continuous experiment 5: Sample 3



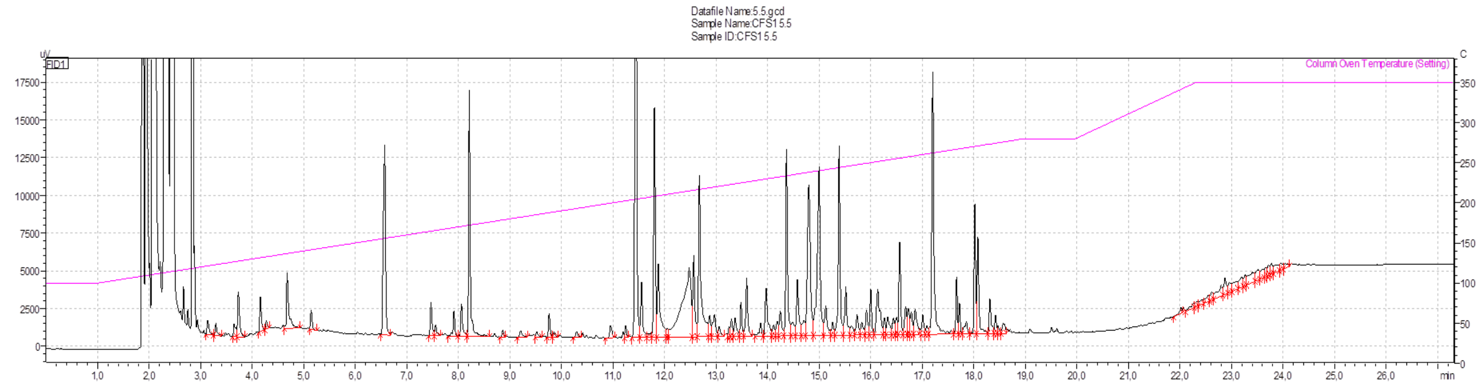
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.691	g/l	80, 81, 82, 83, 84, ...	58511	24879	5.885
2	A	16.024	0.843	g/l	61, 62, 63, 64, 65, ...	114862	44291	11.552
3	C	11.156	5.235	g/l	29, 30, 31, 32, 33, ...	229413	89485	23.073
4	D	13.887	2.684	g/l	43, 44, 45, 46, 47, ...	93431	35090	9.397

Continuous experiment 5: Sample 4



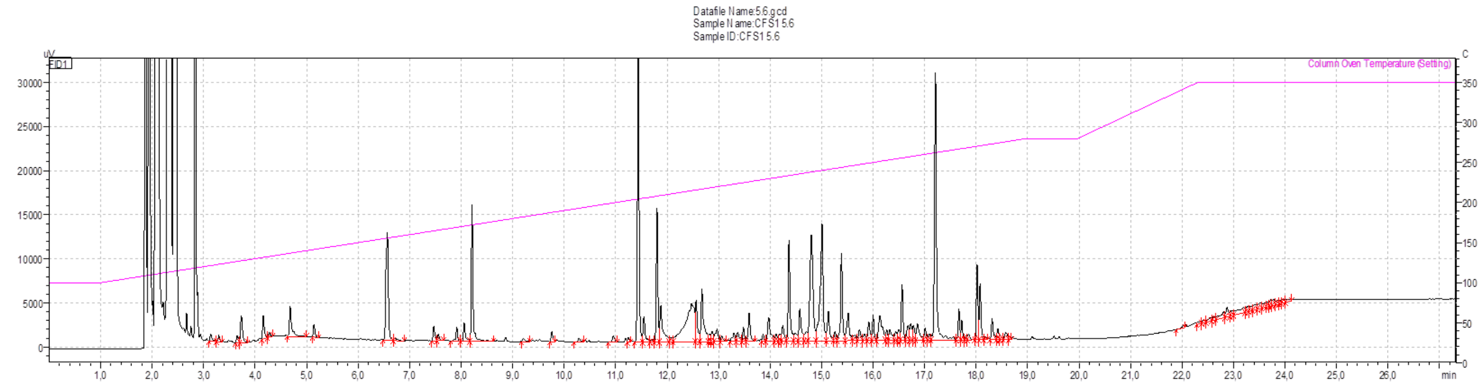
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.846	g/l	74, 75, 76, 77, 78, ...	71619	28074	8.476
2	A	16.024	0.853	g/l	55, 56, 57, 58, 59, ...	116248	41439	13.757
3	C	11.156	3.096	g/l	25, 26, 27, 28, 29	135705	57167	16.06
4	D	13.887	2.582	g/l	38, 39, 40, 41, 42, ...	89891	32734	10.638

Continuous experiment 5: Sample 5



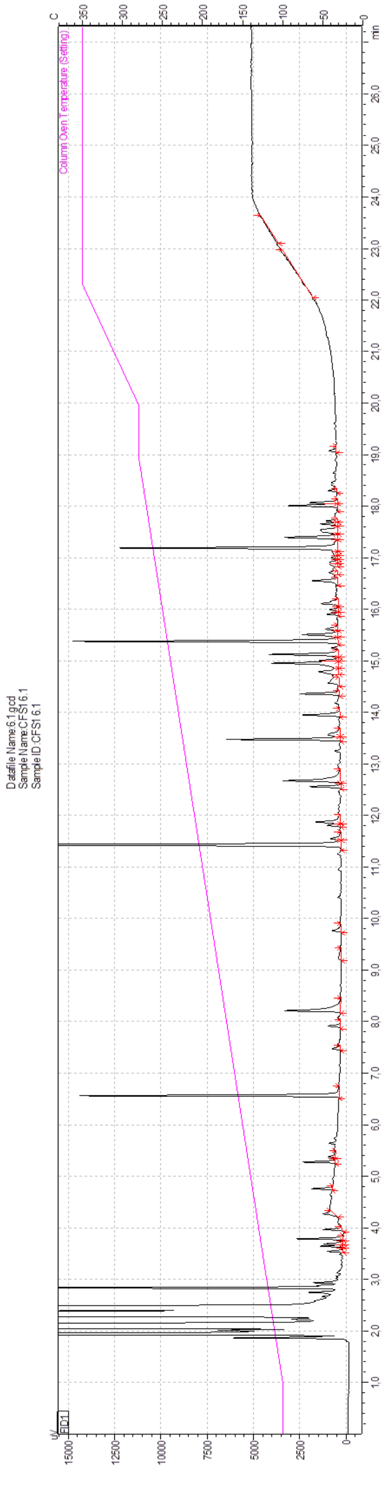
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.326	g/l	72, 73, 74, 75, 76, ...	112283	43342	12.253
2	A	16.024	0.903	g/l	52, 53, 54, 55, 56, ...	123114	42452	13.435
3	C	11.156	2.552	g/l	21, 22, 23, 24, 25	111860	47041	12.207
4	D	13.887	2.709	g/l	35, 36, 37, 38, 39, ...	94302	33340	10.291

Continuous experiment 5: Sample 6



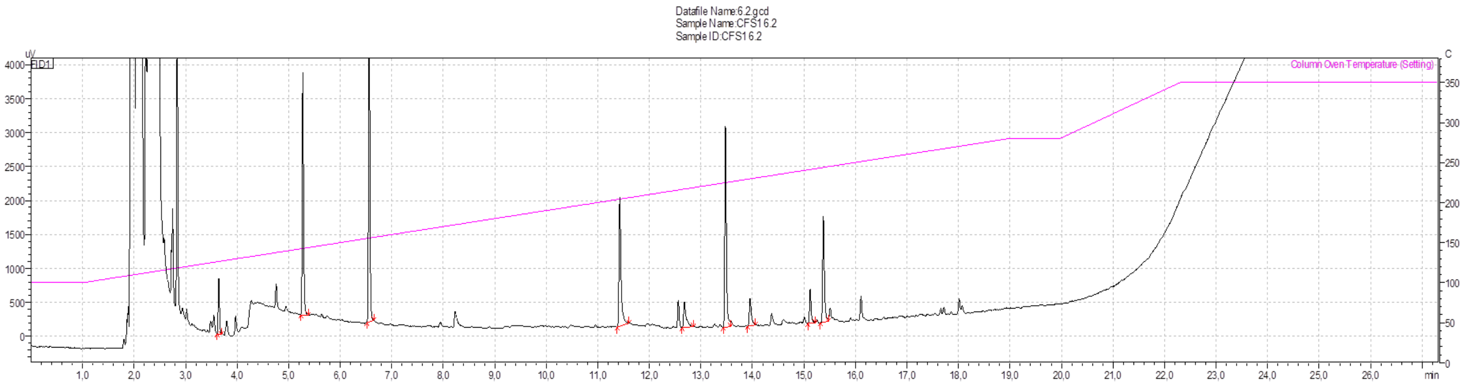
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	1.745	g/l	70, 71, 72, 73, 74, ...	147701	57129	16.182
2	A	16.024	0.89	g/l	50, 51, 52, 53, 54, ...	121354	40507	13.296
3	C	11.156	1.974	g/l	19, 20, 21, 22, 23	86526	36694	9.48
4	D	13.887	2.522	g/l	34, 35, 36, 37, 38, ...	87817	29696	9.621

Continuous experiment 6: Sample 1



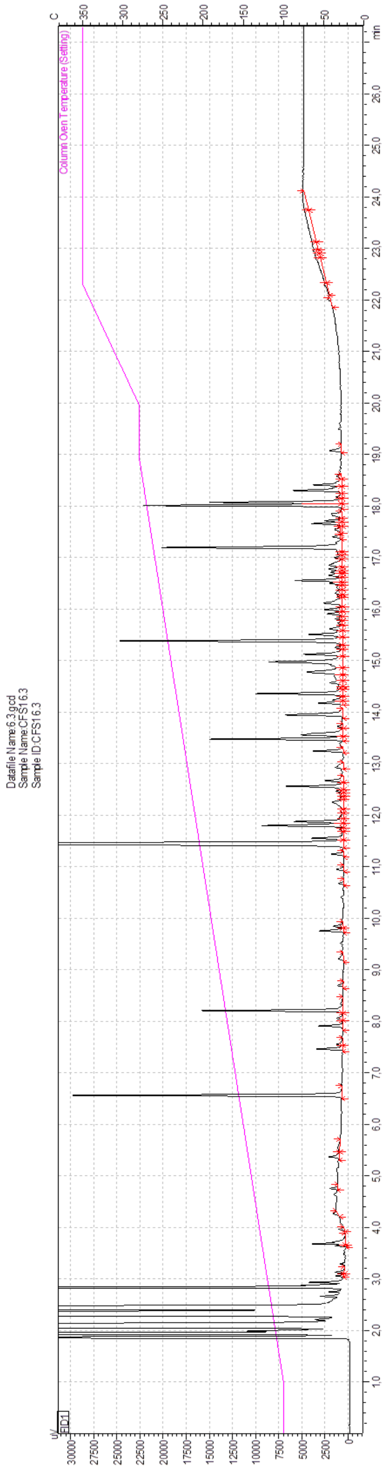
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.617	g/l	43, 44, 45, 46, 47, ...	52257	21596	17.386
2	A	16.024	0.358	g/l	31, 32, 33, 34, 35, ...	48809	20514	16.239
3	C	11.156	1.17	g/l	16, 17	51266	23170	17.057
4	D	13.887	0.833	g/l	22, 23, 24, 25, 26	29009	11480	9.651

Continuous experiment 6: Sample 2



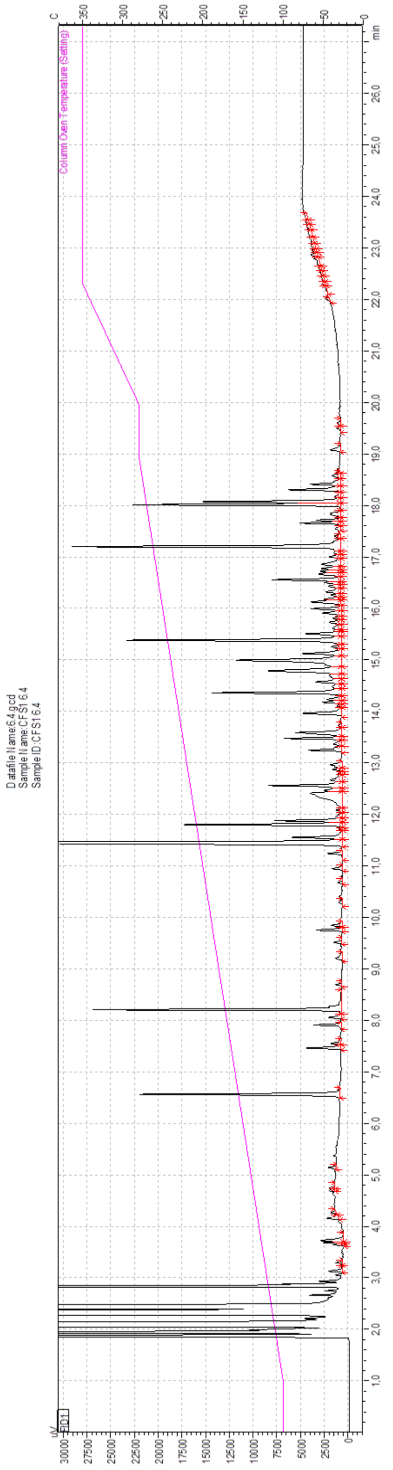
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	No peak is detected.	0	g/l	--	0	0	0
2	A	15.378	0.027	g/l	9	3616	1534	9.774
3	C	11.426	0.116	g/l	4	5081	1890	13.734
4	D	13.887	0.216	g/l	6, 7	7519	3293	20.323

Continuous experiment 6: Sample 3



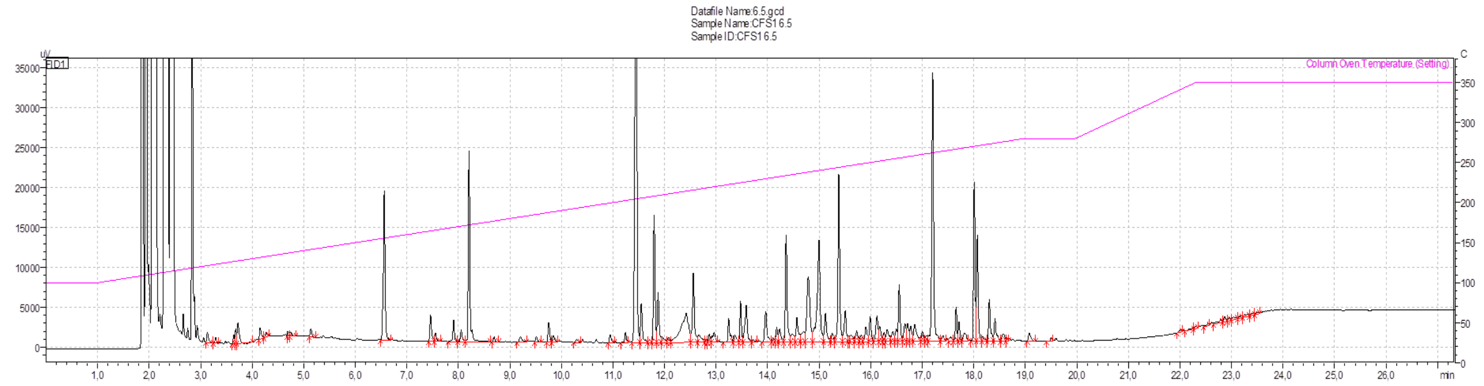
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.012	g/l	71, 72, 73, 74, 75, ...	170284	71650	17.585
2	A	16.024	0.934	g/l	51, 52, 53, 54, 55, ...	127376	48696	13.154
3	C	11.156	5.192	g/l	20, 21, 22, 23, 24, ...	227563	88691	23.501
4	D	13.887	3.175	g/l	37, 38, 39, 40, 41, ...	110538	44218	11.415

Continuous experiment 6: Sample 4



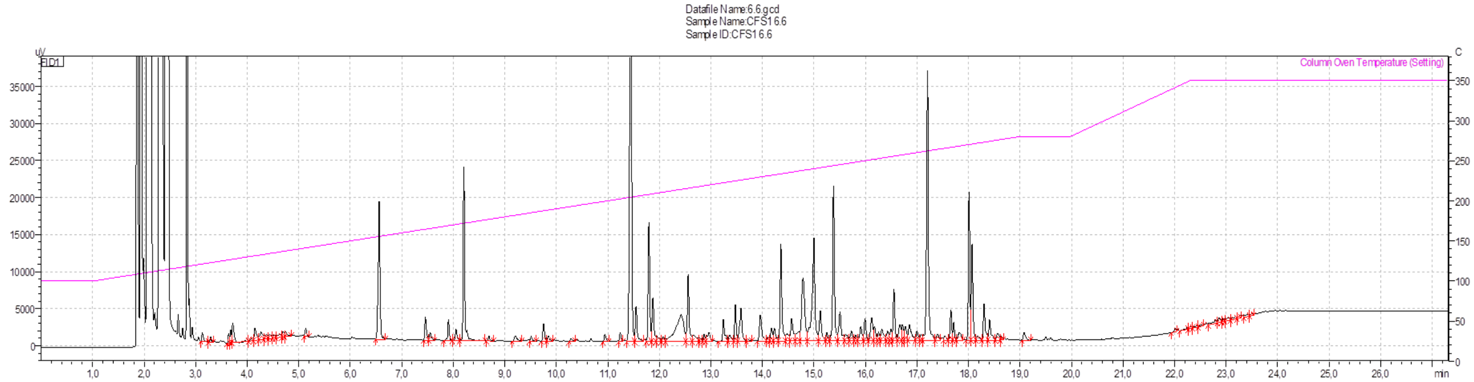
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.449	g/l	78, 79, 80, 81, 82, ...	207352	83630	18.031
2	A	16.024	1.184	g/l	56, 57, 58, 59, 60, ...	161365	60499	14.032
3	C	11.156	5.129	g/l	23, 24, 25, 26, 27, ...	224773	87901	19.546
4	D	13.887	3.27	g/l	40, 41, 42, 43, 44, ...	113852	41221	9.9

Continuous experiment 6: Sample 5



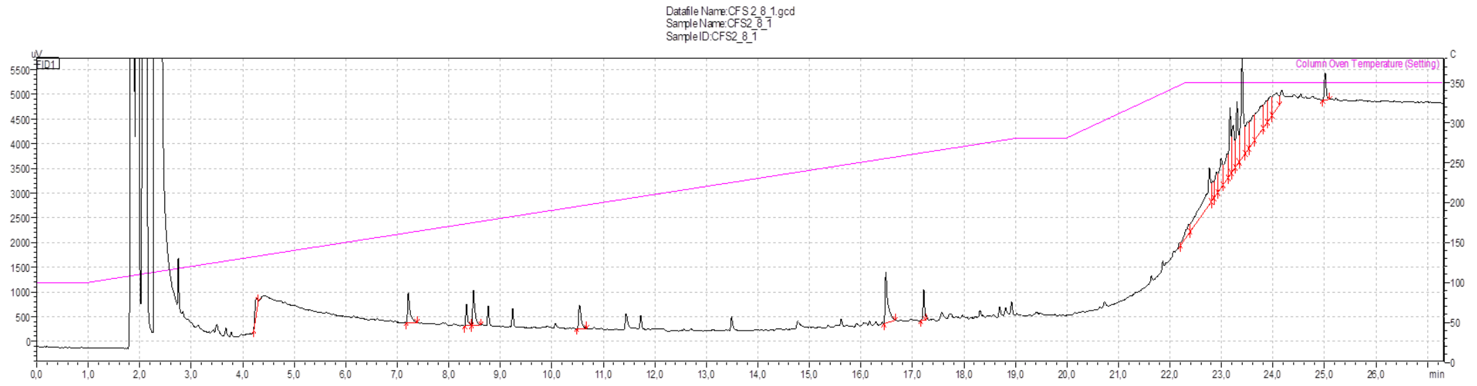
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.468	g/l	76, 77, 78, 79, 80, ...	208965	85024	19.079
2	A	16.024	1.146	g/l	54, 55, 56, 57, 58, ...	156247	58268	14.266
3	C	11.156	4.398	g/l	23, 24, 25, 26, 27	192742	75404	17.598
4	D	13.887	3.111	g/l	38, 39, 40, 41, 42, ...	108314	38988	9.889

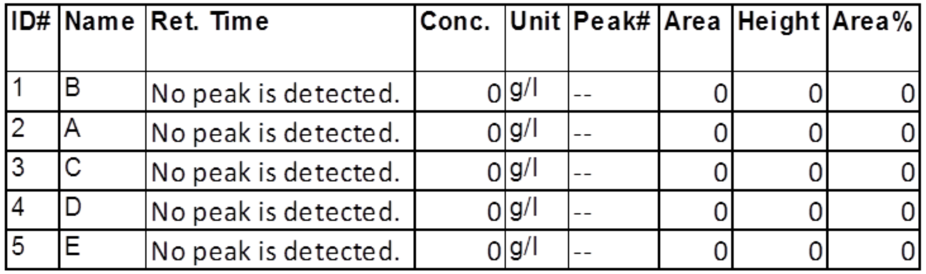
Continuous experiment 6: Sample 6



ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.547	g/l	79, 80, 81, 82, 83, ...	215606	87380	19.391
2	A	16.024	1.151	g/l	58, 59, 60, 61, 62, ...	156867	57090	14.108
3	C	11.156	4.25	g/l	28, 29, 30, 31	186262	76155	16.752
4	D	13.887	3.062	g/l	42, 43, 44, 45, 46, ...	106605	37963	9.588

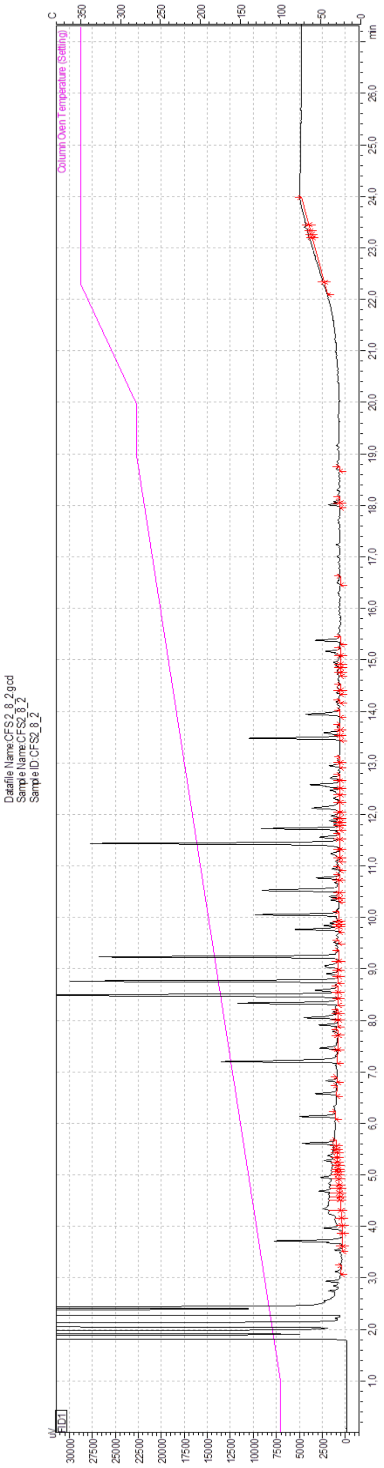
Continuous experiment 8: Sample 1





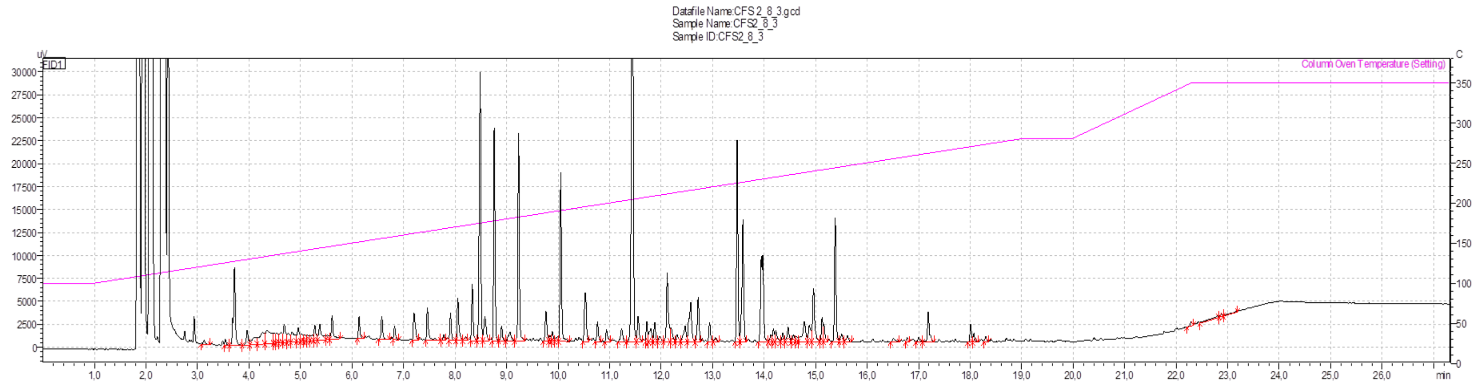
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	No peak is detected.	0	g/l	--	0	0	0
2	A	No peak is detected.	0	g/l	--	0	0	0
3	C	No peak is detected.	0	g/l	--	0	0	0
4	D	No peak is detected.	0	g/l	--	0	0	0
5	E	No peak is detected.	0	g/l	--	0	0	0

Continuous experiment 8: Sample 2



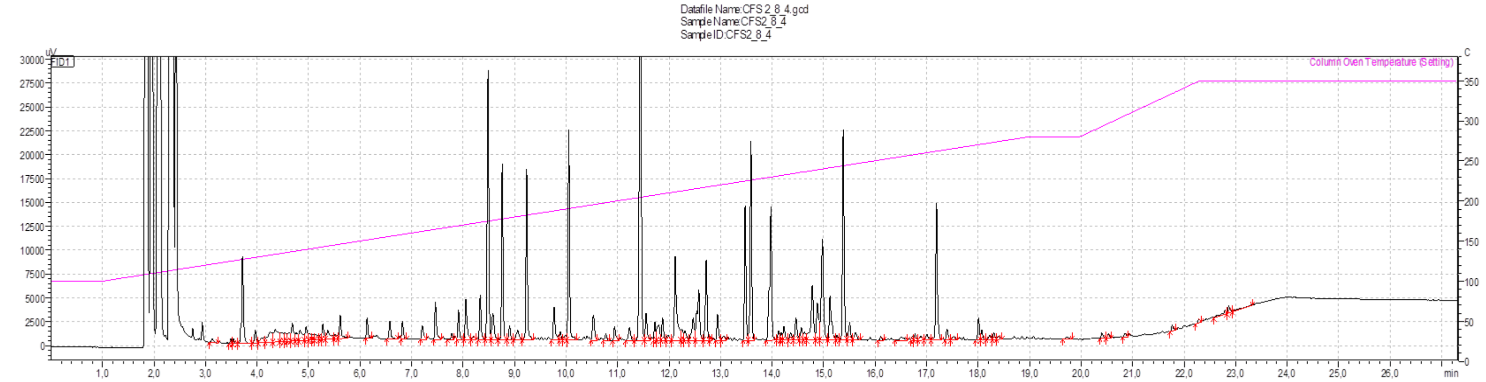
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.061	g/l	78, 79, 80	5180	2239	0.716
2	A	16.024	0.06	g/l	76, 77	8167	3083	1.129
3	C	11.156	2.206	g/l	47, 48, 49, 50, 51, ...	96664	41822	13.363
4	D	13.887	1.163	g/l	64, 65, 66, 67, 68, ...	40493	16863	5.598
5	E	7.18	1.306	g/l	25, 26, 27	39686	15655	5.486

Continuous experiment 8: Sample 3



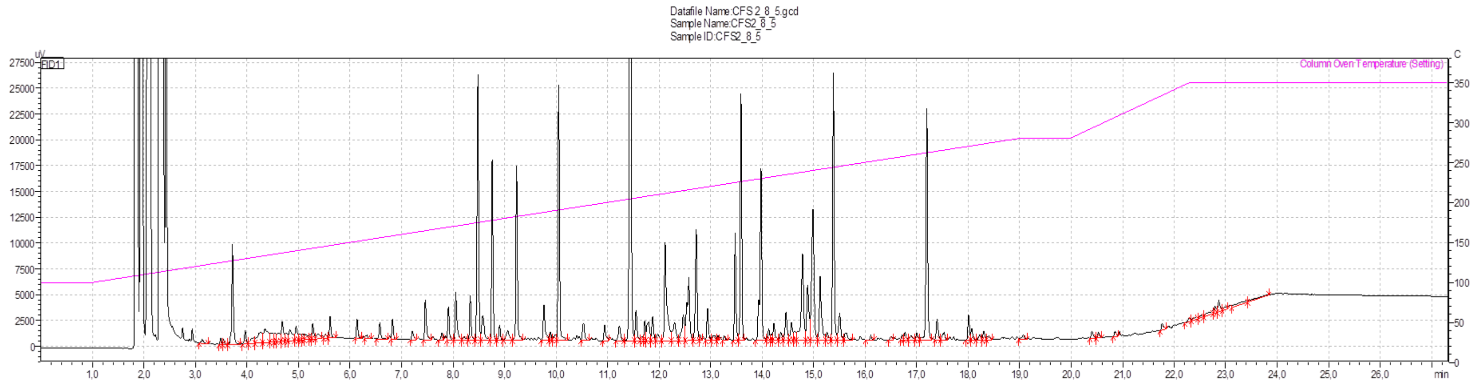
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.202	g/l	83, 84, 85, 86	17076	6766	1.927
2	A	16.024	0.266	g/l	77, 78, 79, 80, 81	36322	15759	4.098
3	C	11.156	3.477	g/l	45, 46, 47, 48, 49, ...	152397	63346	17.195
4	D	13.887	3.795	g/l	62, 63, 64, 65, 66, ...	132108	51203	14.906
5	E	7.18	0.649	g/l	25, 26, 27	19715	7898	2.225

Continuous experiment 8: Sample 4



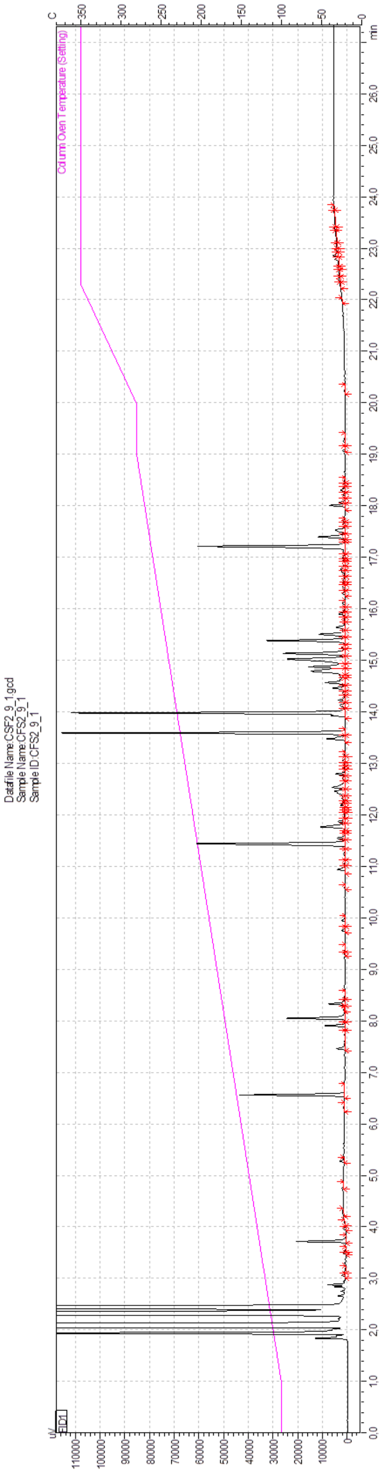
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.597	g/l	87, 88, 89, 90, 91, ...	50519	20606	5.187
2	A	16.024	0.456	g/l	77, 78, 79, 80, 81, ...	62174	26454	6.384
3	C	11.156	3.393	g/l	45, 46, 47, 48, 49, ...	148694	60462	15.268
4	D	13.887	3.811	g/l	63, 64, 65, 66, 67, ...	132687	56346	13.624
5	E	7.18	0.563	g/l	26, 27, 28	17113	7112	1.757

Continuous experiment 8: Sample 5



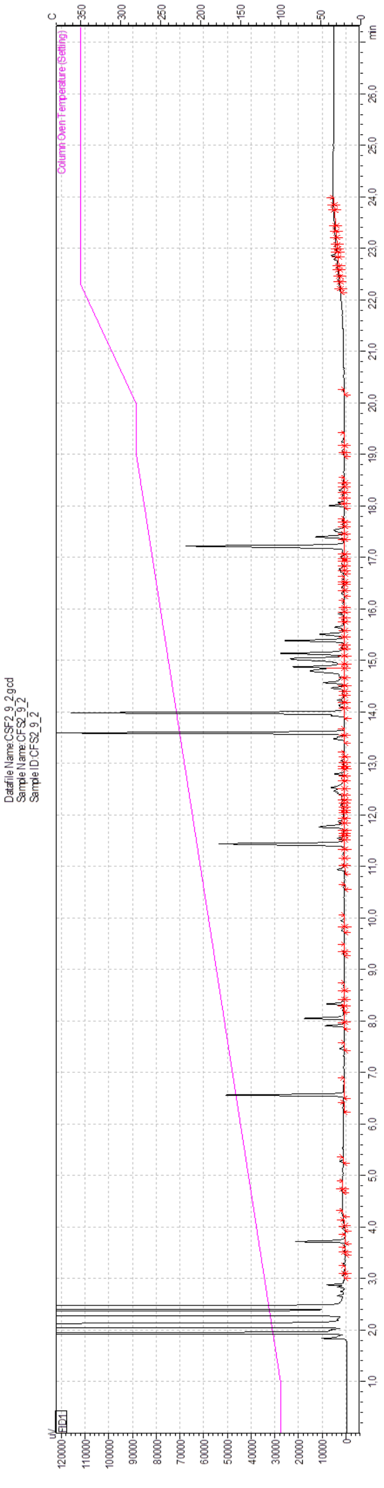
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	0.875	g/l	89, 90, 91, 92, 93, ...	74059	30116	7.107
2	A	16.024	0.552	g/l	79, 80, 81, 82, 83, ...	75194	31735	7.215
3	C	11.156	3.237	g/l	46, 47, 48, 49, 50, ...	141858	58169	13.612
4	D	13.887	3.905	g/l	64, 65, 66, 67, 68, ...	135943	59397	13.045
5	E	7.18	0.517	g/l	27, 28, 29	15728	6604	1.509

Continuous experiment 9: Sample 1



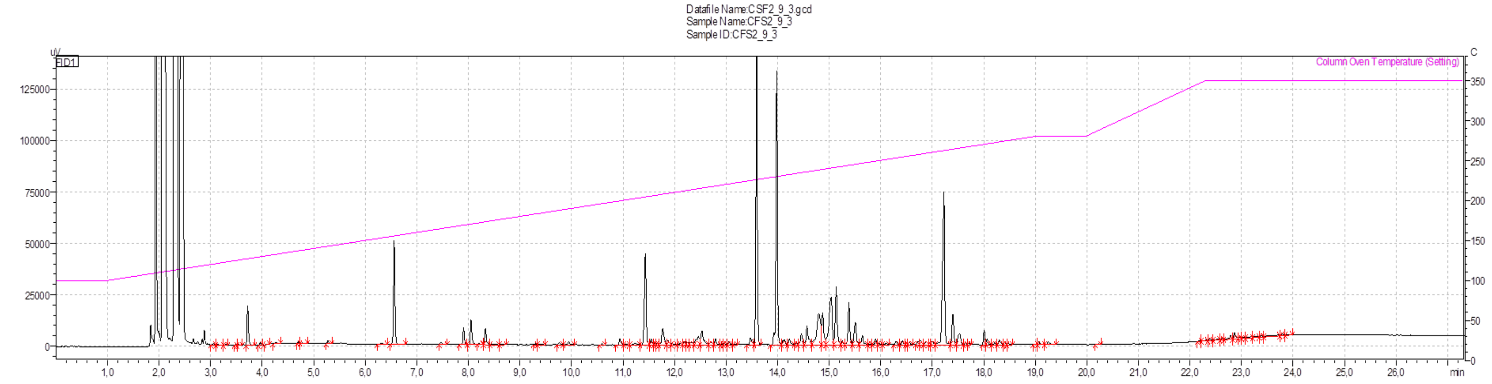
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	2.82	g/l	76, 77, 78, 79, 80, ...	238713	89673	13.074
2	A	16.024	1.177	g/l	59, 60, 61, 62, 63, ...	160498	61533	8.791
3	C	11.156	4.207	g/l	23, 24, 25, 26, 27, ...	184384	69609	10.099
4	D	13.887	15.608	g/l	45, 46, 47, 48, 49, ...	543378	252439	29.761

Continuous experiment 9: Sample 2



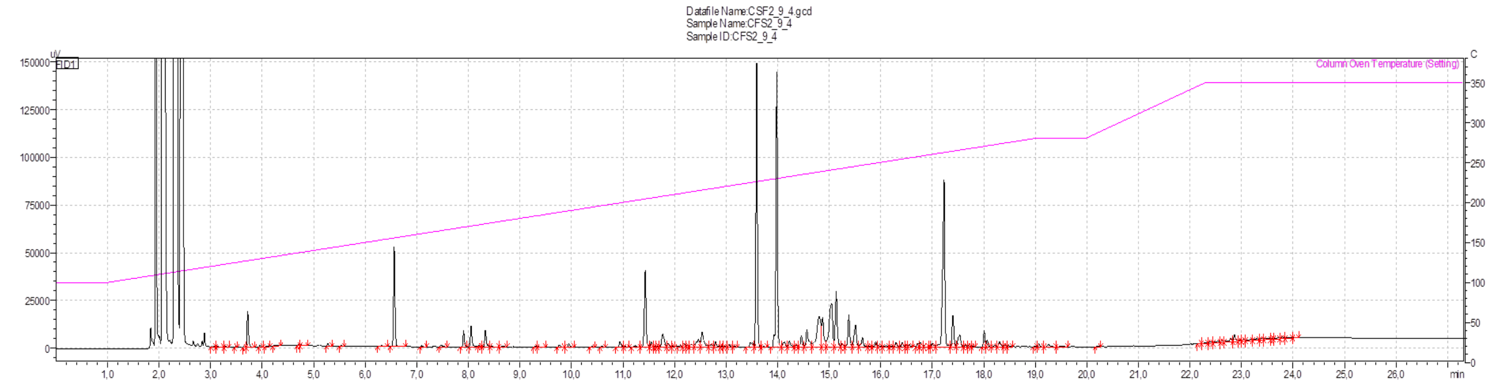
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.219	g/l	78, 79, 80, 81, 82, ...	272518	98825	14.164
2	A	16.024	1.088	g/l	61, 62, 63, 64, 65, ...	148278	54419	7.707
3	C	11.156	3.718	g/l	25, 26, 27, 28, 29, ...	162938	62038	8.469
4	D	13.887	16.654	g/l	49, 50, 51, 52, 53, ...	579777	267788	30.134

Continuous experiment 9: Sample 3



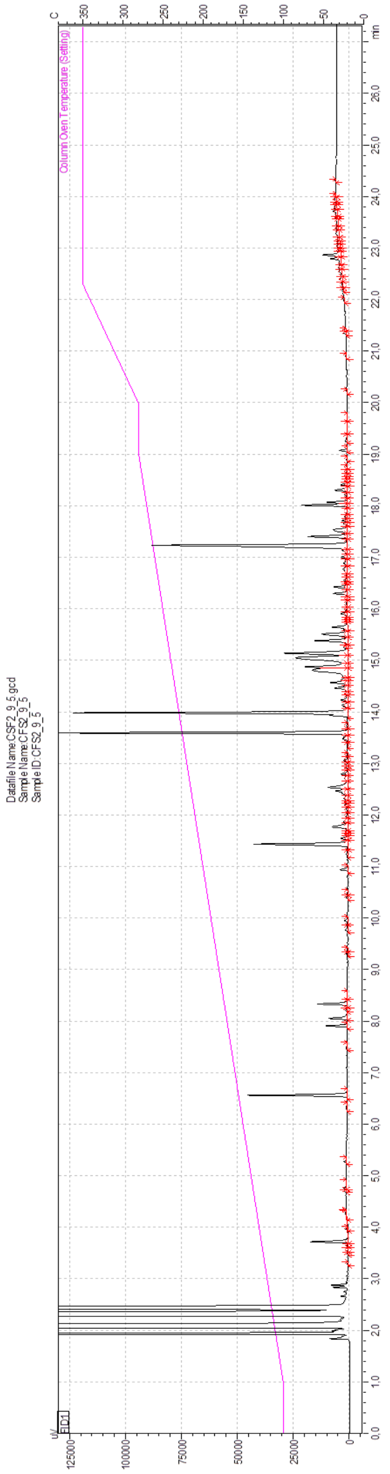
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.748	g/l	78, 79, 80, 81, 82, ...	317320	110910	16.168
2	A	16.024	1.062	g/l	61, 62, 63, 64, 65, ...	144740	52298	7.375
3	C	11.156	3.057	g/l	26, 27, 28, 29, 30, ...	133990	52766	6.827
4	D	13.887	18.128	g/l	49, 50, 51, 52, 53, ...	631112	295498	32.156

Continuous experiment 9: Sample 4



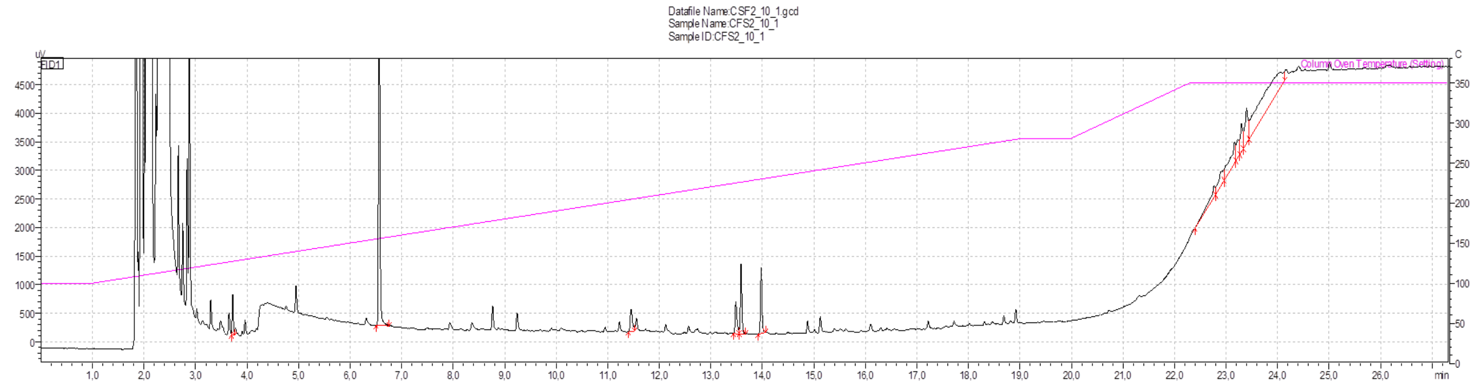
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.363	g/l	83, 84, 85, 86, 87, ...	369348	129340	17.689
2	A	16.024	1.103	g/l	65, 66, 67, 68, 69, ...	150418	51778	7.204
3	C	11.156	2.716	g/l	29, 30, 31, 32, 33, ...	119050	48662	5.702
4	D	13.887	19.229	g/l	52, 53, 54, 55, 56, ...	669433	314342	32.062

Continuous experiment 9: Sample 5



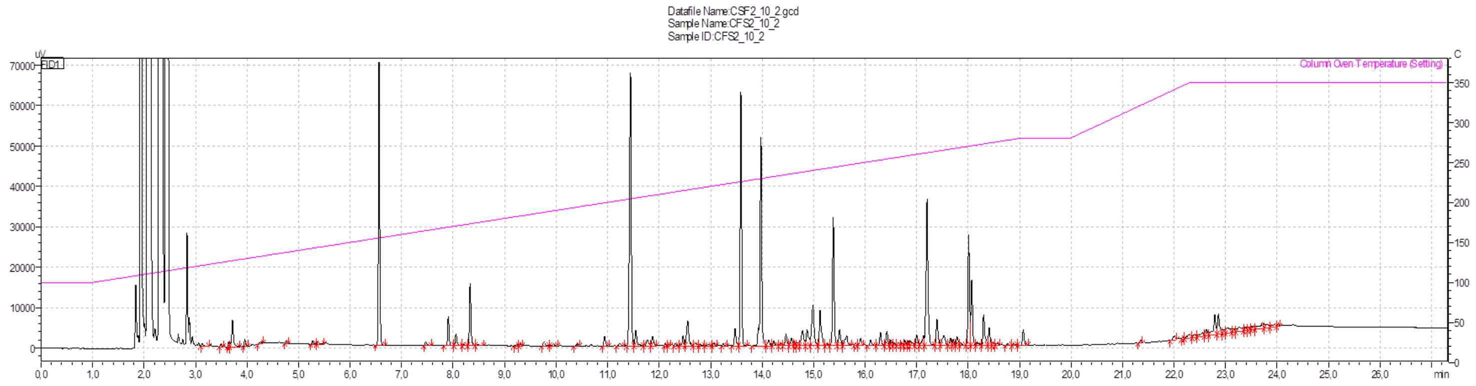
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	5.31	g/l	79, 80, 81, 82, 83, ...	449479	162154	20.537
2	A	16.024	1.239	g/l	61, 62, 63, 64, 65, ...	168914	58277	7.718
3	C	11.156	2.841	g/l	25, 26, 27, 28, 29, ...	124497	50020	5.688
4	D	13.887	16.972	g/l	46, 47, 48, 49, 50, ...	590857	275285	26.996

Continuous experiment 10: Sample 1



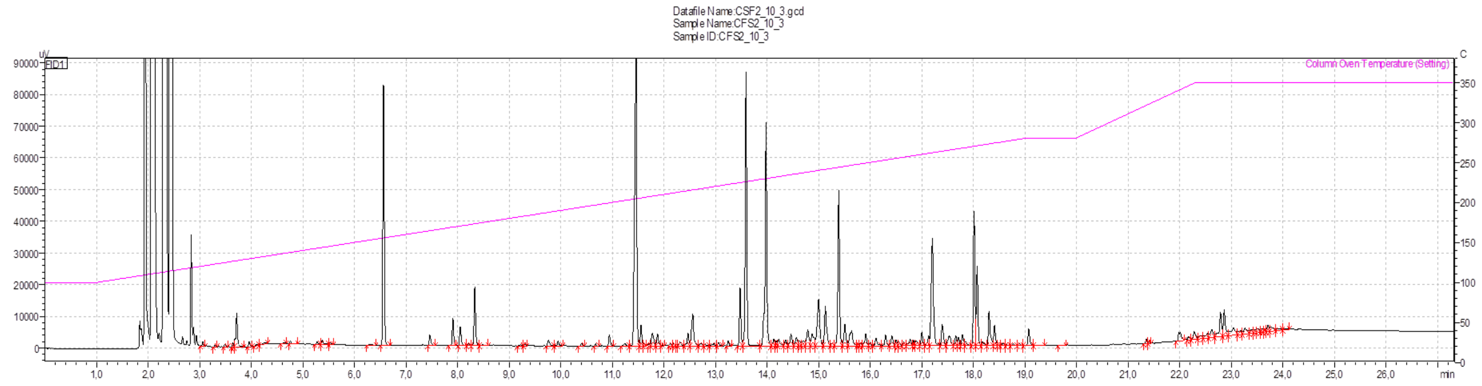
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	No peak is detected.	0	g/l	--	0	0	0
2	A	No peak is detected.	0	g/l	--	0	0	0
3	C	11.453	0.028	g/l	3	1215	384	2.498
4	D	13.887	0.181	g/l	4, 5, 6	6298	2903	12.954

Continuous experiment 10: Sample 2



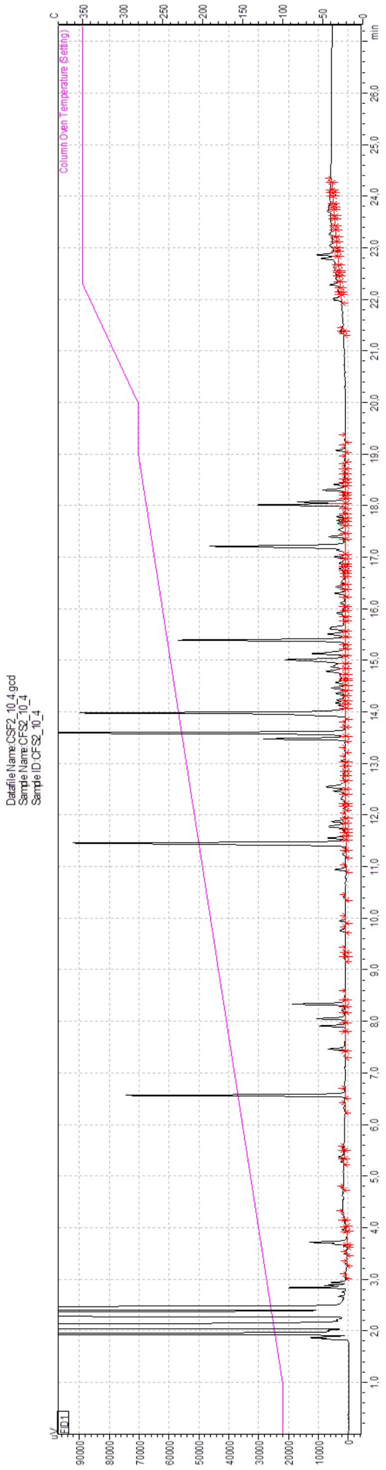
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.275	g/l	69, 70, 71, 72, 73, ...	277218	111544	20.389
2	A	16.024	1.003	g/l	52, 53, 54, 55, 56, ...	136787	54742	10.06
3	C	11.156	4.13	g/l	22, 23, 24, 25	181016	74185	13.313
4	D	13.887	7.842	g/l	37, 38, 39, 40, 41, ...	273009	126805	20.079

Continuous experiment 10: Sample 3



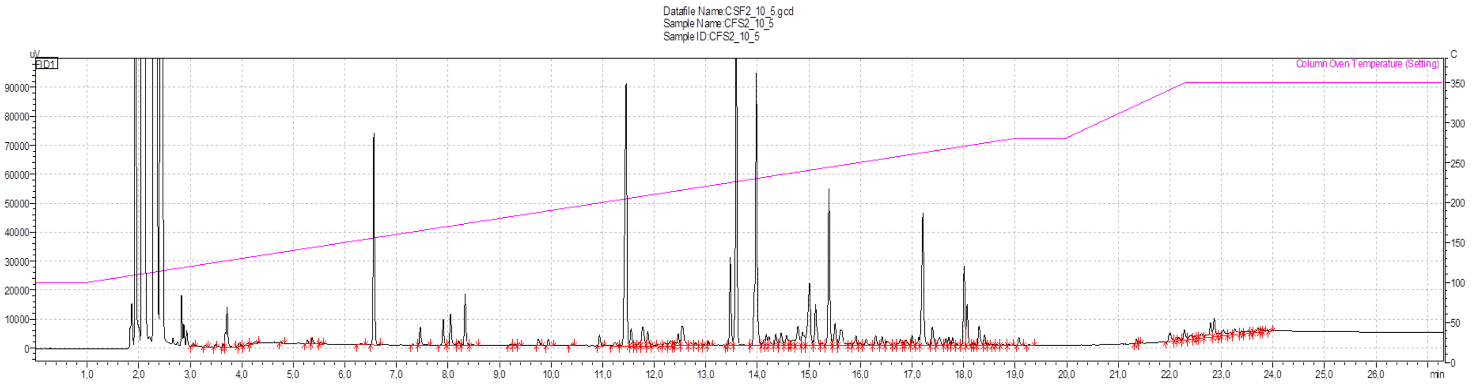
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.44	g/l	81, 82, 83, 84, 85, ...	375878	146684	18.571
2	A	16.024	1.604	g/l	63, 64, 65, 66, 67, ...	218736	84694	10.807
3	C	11.156	6.691	g/l	27, 28, 29, 30, 31, ...	293231	108583	14.487
4	D	13.887	12.16	g/l	47, 48, 49, 50, 51, ...	423323	188415	20.915

Continuous experiment 10: Sample 4



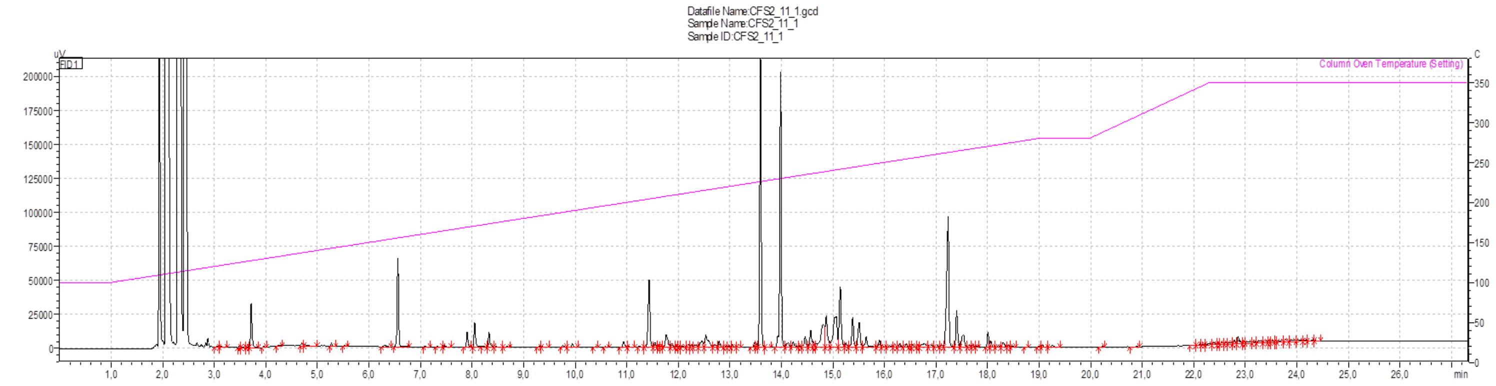
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.745	g/l	81, 82, 83, 84, 85, ...	317065	122681	14.451
2	A	16.024	1.691	g/l	64, 65, 66, 67, 68, ...	230600	88505	10.51
3	C	11.156	6.515	g/l	28, 29, 30, 31, 32, ...	285512	104237	13.013
4	D	13.887	16.199	g/l	47, 48, 49, 50, 51, ...	563936	246734	25.703

Continuous experiment 10: Sample 5



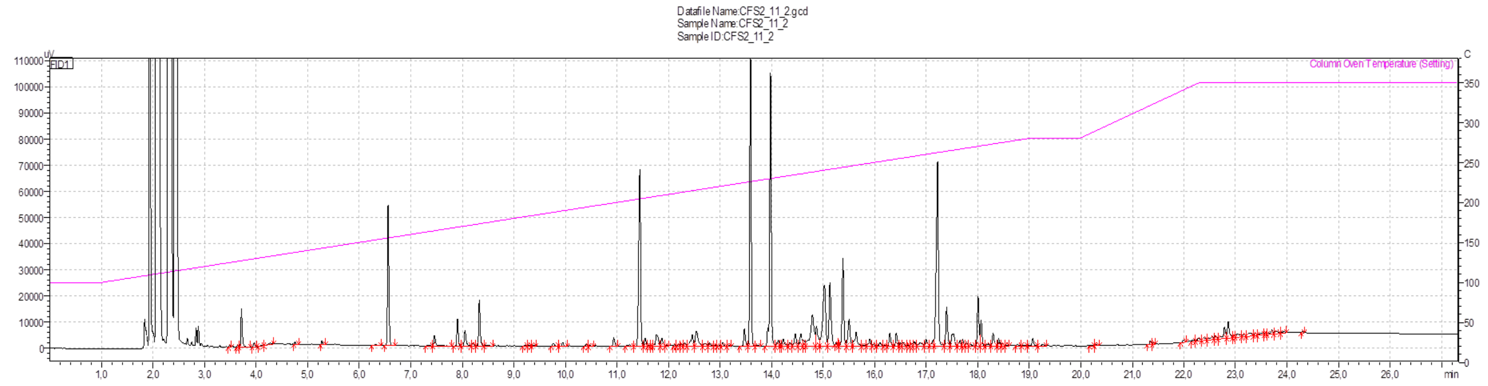
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.636	g/l	80, 81, 82, 83, 84, ...	307771	121481	13.996
2	A	16.024	1.752	g/l	64, 65, 66, 67, 68, ...	238888	88580	10.864
3	C	11.156	6.631	g/l	28, 29, 30, 31, 32, ...	290599	103690	13.215
4	D	13.887	17.221	g/l	48, 49, 50, 51, 52, ...	599543	262927	27.265

Continuous experiment 11: Sample 1



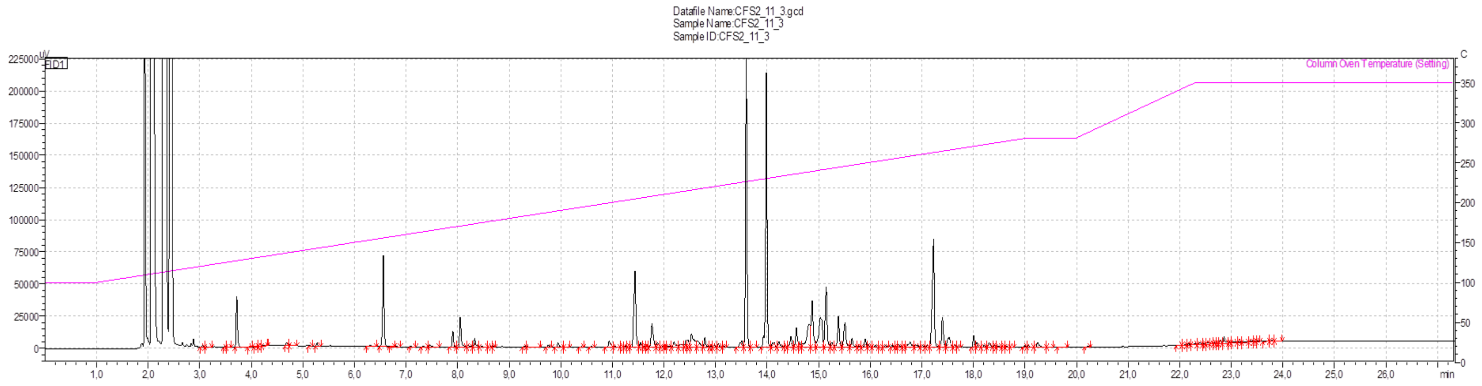
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	5.472	g/l	84, 85, 86, 87, 88, ...	463246	160270	16.209
2	A	16.024	1.508	g/l	68, 69, 70, 71, 72, ...	205629	70818	7.195
3	C	11.156	3.624	g/l	29, 30, 31, 32, 33, ...	158828	61615	5.557
4	D	13.887	26.993	g/l	53, 54, 55, 56, 57, ...	939743	442942	32.881

Continuous experiment 11: Sample 2



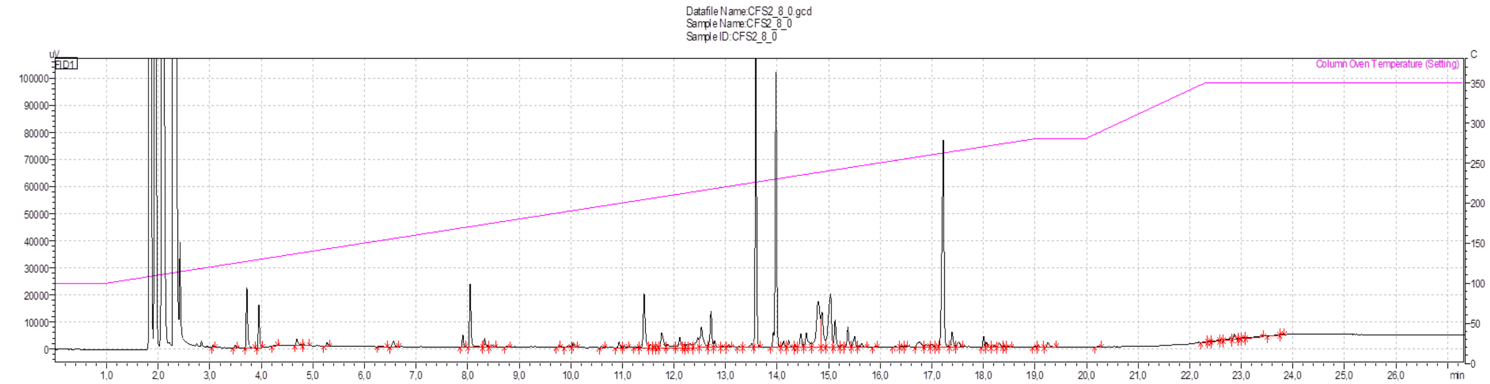
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.464	g/l	79, 80, 81, 82, 83, ...	377880	139588	18.687
2	A	16.024	1.4	g/l	61, 62, 63, 64, 65, ...	190899	71697	9.44
3	C	11.156	4.388	g/l	25, 26, 27, 28, 29, ...	192310	75643	9.51
4	D	13.887	14.773	g/l	46, 47, 48, 49, 50, ...	514307	242291	25.434

Continuous experiment 11: Sample 3



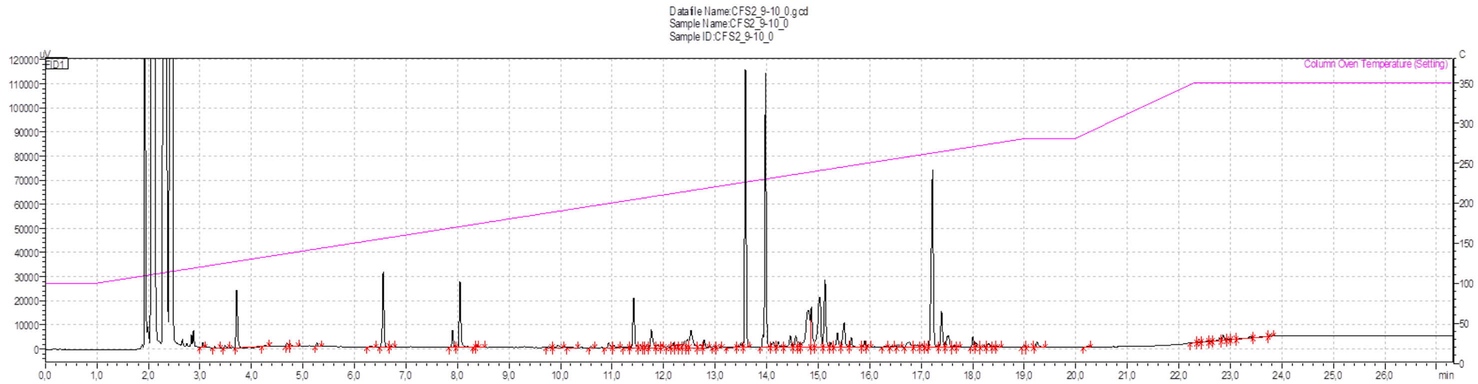
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.607	g/l	90, 91, 92, 93, 94, ...	389957	139456	13.139
2	A	16.024	1.57	g/l	73, 74, 75, 76, 77, ...	214076	74251	7.213
3	C	11.156	4.687	g/l	33, 34, 35, 36, 37, ...	205401	73255	6.921
4	D	13.887	28.213	g/l	59, 60, 61, 62, 63, ...	982192	470392	33.093

Continuous experiment 8: Raw material



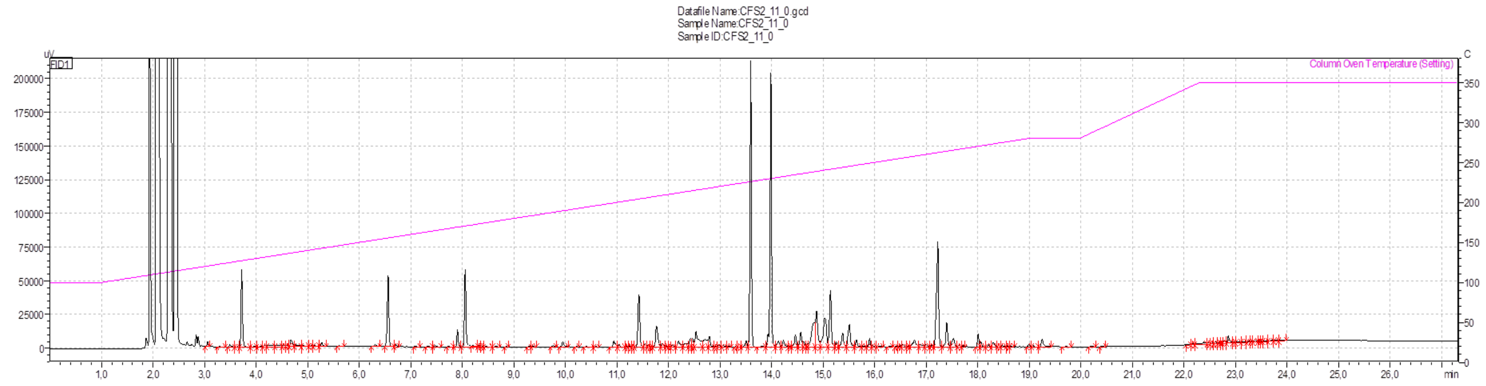
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.094	g/l	63, 64, 65, 66, 67, ...	261883	93639	17.956
2	A	16.024	0.418	g/l	52, 53, 54, 55, 56, ...	57048	17552	3.911
3	C	11.156	1.53	g/l	19, 20, 21, 22, 23, ...	67067	25145	4.598
4	D	13.887	13.458	g/l	39, 40, 41, 42, 43, ...	468508	224307	32.122
5	E	No peak is detected.	0	g/l	--	0	0	0

Continuous experiment 9–10: Raw material



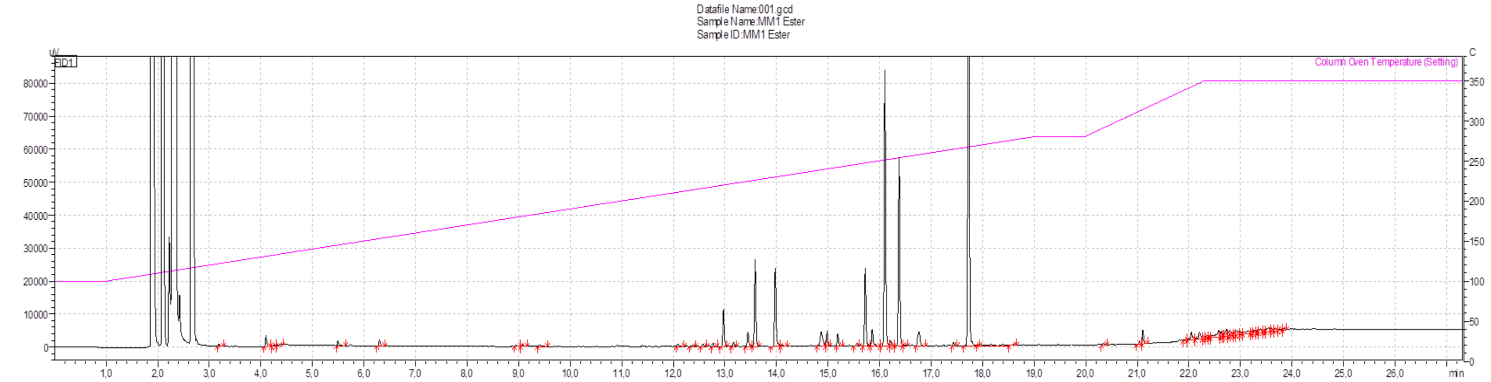
ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.439	g/l	66, 67, 68, 69, 70, ...	291106	105128	17.965
2	A	16.024	0.689	g/l	54, 55, 56, 57, 58, ...	93950	30569	5.798
3	C	11.156	1.516	g/l	19, 20, 21, 22, 23, ...	66451	26747	4.101
4	D	13.887	14.519	g/l	41, 42, 43, 44, 45, ...	505467	242860	31.193
5	E	No peak is detected.	0	g/l	--	0	0	0

Continuous experiment 11: Raw material



ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	4.246	g/l	100, 101, 102, 103, 104, …	359427	126185	12.188
2	A	16.024	1.305	g/l	84, 85, 86, 87, 88, …	177914	56430	6.033
3	C	11.156	3.243	g/l	41, 42, 43, 44, 45, …	142128	52686	4.819
4	D	13.887	27.349	g/l	67, 68, 69, 70, 71, …	952104	446126	32.285
5	E	7.18	0.151	g/l	23, 24, 25	4599	1591	0.156

Continuous experiments 8–11: Raw material before the experiments



ID#	Name	Ret. Time	Conc.	Unit	Peak#	Area	Height	Area%
1	B	18.025	3.398	g/l	31, 32, 33, 34	287678	140679	30.374
2	A	16.024	2.612	g/l	23, 24, 25, 26, 27, ...	356132	173741	37.602
3	C	No peak is detected.	0	g/l	--	0	0	0
4	D	13.887	3.239	g/l	16, 17, 18, 19	112753	54607	11.905
5	E	No peak is detected.	0	g/l	--	0	0	0