Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences

Hammad Ali

Conversion of Biomass to Aviation Fuel by Hydropyrolysis and Vapors Upgrading.

Master's thesis in Sustainable Chemical and Biochemical Engineering
Supervisor: De Chen
Co-supervisor: Petter Tingelstad
July 2023

NTNU
Norwegian University of
Science and Technology

Hammad Ali

Conversion of Biomass to Aviation Fuel by Hydropyrolysis and Vapors Upgrading.

Master’s thesis in Sustainable Chemical and Biochemical Engineering
Supervisor: De Chen
Co-supervisor: Petter Tingelstad
July 2023

Norwegian University of Science and Technology
Faculty of Natural Sciences

NTNU
Norwegian University of
Science and Technology

Master Thesis TKP 4901

Catalysis Group

Title of Project: **Conversion of Biomass to Aviation Fuel by Hydropyrolysis and Vapors Upgrading.**

Written by: **HAMMAD ALI**

Supervisors: **De Chen**

Co-supervisor: **Petter Tingelstad**

Department of Chemical Engineering

Faculty of Natural Sciences and Technology

NTNU Norwegian University of Science and Technology

Table of Contents:

Gratitude:

I would like to thank my supervisor Professor De Chen at the Department of Chemical Engineering, NTNU for allowing me to work on this project named “**Conversion of biomass to aviation fuel by hydropyrolysis and vapors upgrading**” in collaboration with **Quantafuel** and **Sintef Energi**.

I also want to thank my co-supervisor Ph.D. Petter Tingelstad for his continuous support and guidance throughout the project. He was always there to guide me through whenever I was stuck at any point.

Along with them, I also want to thank Ph.D. candidate Kishore Rajendran and exchange Ph.D. candidate from India Nikhil Kumar for their support throughout the time. Their support also helped me a lot in tackling problems that arose during experimentation.

Finally, I want to mention my family who believed in me, especially my father, the belief they have in me that I would do well, motivated me over time so thank you for your efforts, and father, you will always be in my prayers.

List of Tables:

List of Figures:

Abstract:

The world is moving towards more sustainable energy generation techniques and renewable energy sources, there has been a dire need for alternatives to come into play now and enormous studies have already been done for biofuels as an alternative. The main reason for this greener change is the alarming environmental crisis and global warming along with depleting resources for fossil fuels and the fast-growing population are all reasons and motivations to find an alternative source of energy to fulfill the needs of usage.

Physical changes were made to the rig arrangement to run experiments. One of the main purposes is to increase the overall mas yield for the pilot plant. Two additional glass condensers were attached after the primary condenser and the solvent bottle having GVL was also attached to capture vapors passing through the condensers and not condensed. Overall mass yield was increased from 65% to 90% and bio-oil yield was also increased from 22% to 34% and stabilized for all experiments performed with additional condensers.

Several catalysts were tested for catalytic upgrading ability, analyzing bio-oil samples for composition and carbon chain lengths. Titanium dioxide was used as catalyst support and ruthenium, platinum, and cobalt were used as active metals for catalysts. Gas analysis showed CO, CO_2, CH_4, and light hydrocarbons C_2- C_6 were present with CO and CO_2 being the main contributors. Ketonization and aldol condensation reactions took place in the presence of catalysts. (FCC + Co/TiO_2 + Pt/TiO_2) has shown good ketonization activity following (FCC + Ru/TiO_2). Pure titanium dioxide has shown high hydrogenation ability as well. Sand and FCC were used as the fluidizing medium in the pyrolysis reactor.

Elemental analysis to identify carbon, oxygen, and hydrogen present in bio-oil was also done and a comparison was documented with conventional diesel fuel. H/C and O/C ratios were also plotted on van Krevelen's diagram to visualize the conditions and differences of the sample from conventional fuel. HHV was also calculated for bio-oil and compared with diesel fuel, the difference is noted as there is a difference in elemental composition for samples analyzed.

Abbreviations:

GHG:	Greenhouse gases
GVL:	g-valerolactone
GC FID:	Gas Chromatography Flame Ionization Detector
GC TCD:	Gas Chromatography Thermal Conductivity Detector
GC-MS:	Gas Chromatography-Mass Spectrometry
FHP:	Fast hydropyrolysis
HDO:	Hydrodeoxygenation
HTL:	Hydrothermal liquefaction
HTG:	Hydrothermal gasification
KF:	Karl Fischer
SEM:	Scanning electron microscopy
TEM:	Transmission electron microscopy
BET:	Brunauer Emmet Teller
XRD:	X-ray diffraction
FCC:	Fluid catalytic cracking
PHT:	Pressure holdup test

1. Introduction:

Renewable energy sources have become an important contributor today to supply energy as without renewable energy, it might be difficult to sustain the environment from a carbon footprint and to achieve UN sustainability targets. Although there are limitations to using specific energy sources but biomass on the other hand is a more reliable source to produce fuels primarily liquid and gaseous products along with solid products as well and it can be transported easily anywhere if not present locally. Also, with growing population and depleting fossil reserves also indicating us to find another solution to generate energy utilizing different sources. In Europe specifically, more focus is on hydrogen, ammonia, biomass, and plastics as alternatives to use for energy generation[4].

The main focus of the Paris agreement is to cut down emissions and to limit the global temperature rising by 1.5^{o}C. Partner countries from the agreement agreed to work to have new projects in place and to reduce GHG (greenhouse gases) by having renewable energy sources as the main energy provider but the current dynamics and projects timeline has shifted because of the war that Russia started in Ukraine as Russia is a main supplier of natural gas to many European countries and now they are focused to switch towards renewable energy projects faster than initially planned to tackle down gas shortage and to run industries as usual but it's hard to say whether it's possible to switch towards renewables on a bigger scale in shorter time. The main contributor to carbon emissions in the environment comes from heat and electricity generation, agriculture, transportation, and manufacturing industries, and globally CO_2 makes up 76% of total GHG emissions. By using renewable energy, emissions can be reduced from major contributors like heat and electricity, and transportation[5].

Norway is working towards achieving sustainability in the manufacturing sector and with strict policies by the government, more EVs (electric vehicles) have been sold in 2022 than in previous years showing a positive attitude towards adopting change in cutting down emissions from transportation and ensuring green transition[5].

The project is mainly focused on producing aviation fuels using biomass (beech wood) as raw material and has liquid, gaseous, and solid products which are typical products obtained from the pyrolysis process. The process configuration for the pilot plant used for the experimentation is a pyrolysis reactor with vapors upgrading reactor holding catalysts for upgradation. Different catalysts have been tested before including ZSM-5, Y-zeolite, Pt/TiO_2, and Ru/TiO_2 and results have been generated to see the catalyst's effect on pyrolysis vapors. With the existing configuration, certain changes have been made to improve the condensation of the vapors by including additional condensers along with using solvent GVL (g-valerolactone) to capture vapors that have not been condensed in condensers.

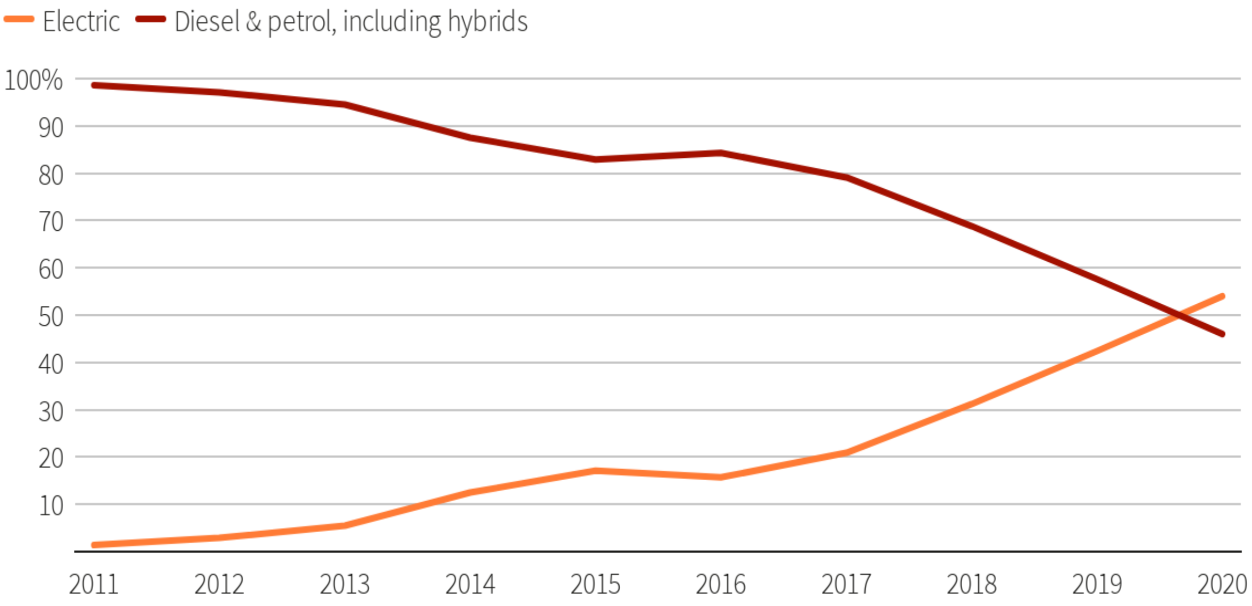


Figure 1: Diesel and electric sales comparison [2].

The main focus during this period given to increase the overall mass yield of the pilot plant along with increasing the runtime as there has been pressure build-up upstream of the gas filter faced during the autumn semester. Also, as several catalysts have been tested, Ru/TiO2 is mainly studied to check the activity of the catalyst and to analyze if it’s achievable to have the catalyst activity for more than 50 hours of runtime after having good results in terms of activity. FCC (fluid catalytic cracking) catalyst was also used in place of sand as a fluidizing medium to have an additional catalytic activity and experiments were also performed without catalysts in upgrading the reactor to have a comparative study about the activity of FCC with sand as fluidizing medium.

The samples obtained were analyzed for gas and liquid phase analysis for compounds having different carbon chain lengths and to analyze the O/C (oxygen to carbon) and H/C (hydrogen to carbon) ratios of bio-oil obtained as it is an important point to see the difference in oxygen content of oil obtained using upgrading catalyst. GC FID and GC-MS were used for the analysis part and to develop methods for analysis in GC FID. The aqueous phase obtained from the experiments was analyzed for water content from Karl Fischer's Titration. A rotary evaporator is also used to separate bio-oil from acetone which is collected by cleaning up the condensers.

1.1. Scope:

The scope of this thesis is a continuation of the previous semester's work, and the main focus of the thesis is:

- To make physical changes primarily in the condensation section to achieve good condensation and capture more vapors increasing the overall mass yield of the pilot plant.
- To check the catalytic activity of catalysts prepared using noble metals on titanium dioxide have a comparative study about their upgrading ability.
- To check the lifetime stability of Ru/TiO_2 for several runs by using the same catalyst without regenerating the catalyst and analyzing samples obtained.
- The characterization of catalysts was outside the scope of this thesis, and it was done by another master's student working on a similar topic, although characterization techniques were studied, and training was provided.

1.2. Thesis structure:

The thesis structure is explained below:

- **Chapter 1** is an introduction to the thesis and the scope of the thesis.
- **Chapter 2** gives details about raw materials and an explanation of their different properties for them.

- **Chapter 3** gives details about conversion techniques to convert biomass into fuel including pyrolysis and different types of pyrolysis and its product distribution.
- **Chapter 4** gives a literature review of hydropyrolysis, reactions occurring during the process, mechanistic model, reactors used, and bio-oil upgrading. Parameters affecting the process were also discussed in this chapter.
- **Chapter 5** gives theoretical information about the types of equipment used for analysis, chemicals used during experiments, a literature review about catalysts, and characterization techniques. Catalysts synthesis and steps to follow are also discussed in this chapter.
- **Chapter 6** gives details about the pilot plant and different sections of the pilot plant.
- **Chapter 7** gives details about the working of the pilot plant and procedures explained for running the experiments, cleaning the rig after experiments, and procedures for the analysis of samples.
- **Chapter 8** is about results obtained from analyzing samples for gases and liquids.
- **Chapter 9** is the conclusion from the results of the thesis.
- **Chapter 10** is about future work that can be done to achieve final products.

2. Raw Materials:

The typical raw materials used for the pyrolysis process and currently being studied are:

- Plastics.
- Biomass.

2.1. Plastics:

Plastics have been used enormously for the pyrolysis process because of their composition to produce bio-oil with low oxygen content primarily hydrocarbons and are available in large amounts which can be recycled to produce fuels. With the increasing population, plastic production also increased to cover the needs and the waste amount increasing particularly in oceans, using it as raw material, and recycling it back will help bring down the waste plastics from the environment. The plan from the environmental organizations to push governments to recycle plastics as much as possible and below is a comparison of plastics flow to different sections between 2016 and 2030 (predictions based on current trends)[3].

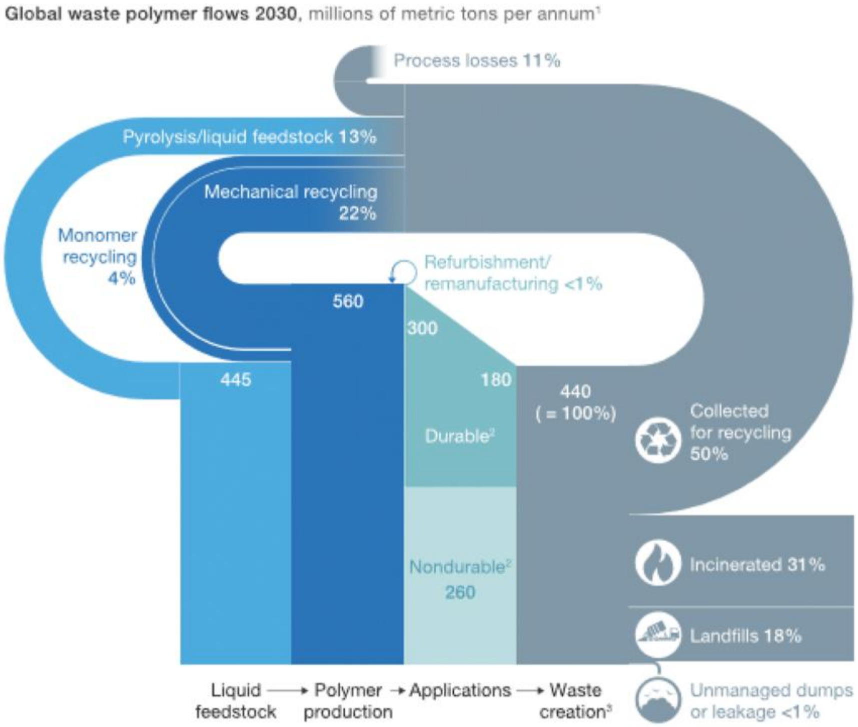


Figure 2: Global plastics flow cycle for 2030 [3].

With the main focus on recycling, it is planned to utilize more than 50% of collected plastics to be recycled for different purposes[3].

2.2. Biomass:

Biomass is also used as raw material to produce fuel, depending on the availability of it, and using non-edible biomass to produce biofuels is the main focus. Several sources can be used as raw materials including plants, waste from crops, and wood as well. The energy share from biomass in 2012 was 49 EJ and it is around 560 EJ, which clearly shows the usage of biomass as an energy producer. With good governance and policies from the government to switch to renewable energy, it is estimated that by 2035 there will be 5% of agricultural land being focused to grow energy crops for liquid fuels and as fuel to generate energy[6] [1].

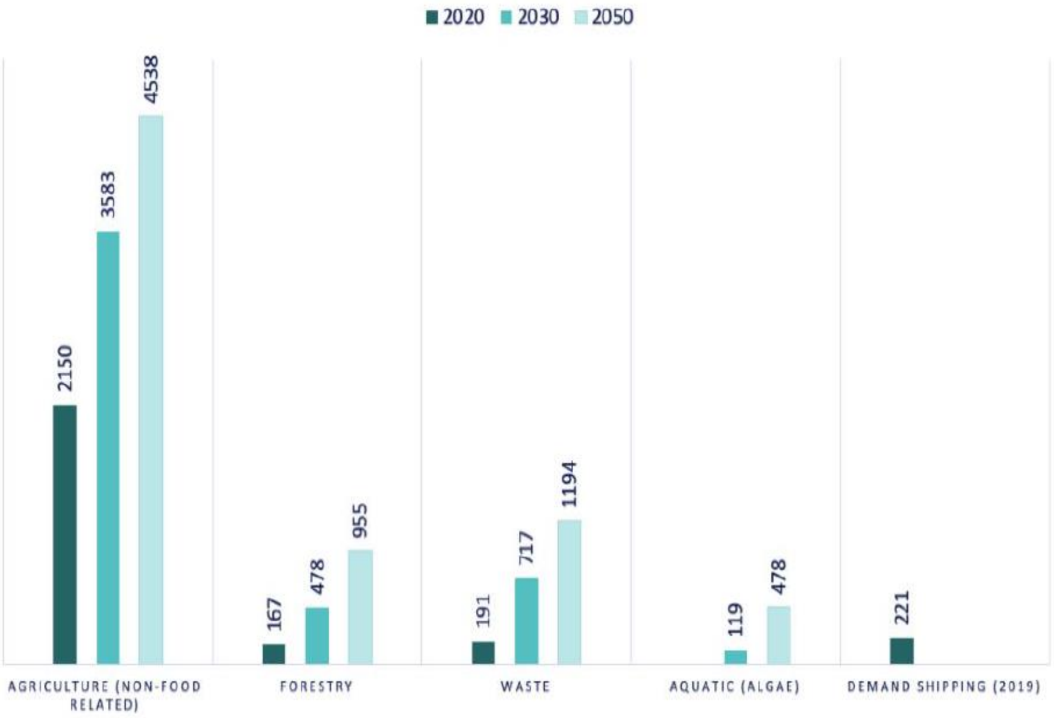


Figure 3: Biomass consumption for energy generation in different sectors [1].

Biomass primarily consists of cellulose, hemicellulose, and lignin, the compositions consist of 40-60%, 20-40%, and 10-24% of respective cellulose, hemicellulose, and lignin. Mostly cellulose and hemicellulose are the main contributors towards bio-oil compounds and lignin promotes furan compounds in bio-oil. Food processing residue is also a main source of biomass availability and the potential availability of biomass for energy generation is growing with dedicated land to grow energy crops[4].

2.2.1. Beech Wood:

Beech wood is commonly named Fagus Grandifolia; this wood is commonly used as raw material for the production of bio-oil. The suitability of beech wood for the pyrolysis process was studied by research groups through thermochemical routes. The most common is the pyrolysis process along with other processes explained below. Particle size is normally in the range of 50μm to 500μm and it varies depending on the requirement for experimental setup. Biomass needs to be analyzed for moisture before it can be used, and the ultimate and proximate analysis showed that there is around 9% moisture and 15% fixed carbon[7].

Figure 4: Beech wood used for experiments.

The ultimate analysis of biomass also gives information about the elemental composition in it. Table 1 below gives information about the elements present in biomass. It is clear from the analysis that carbon and oxygen are the main constituents of biomass with small amounts of hydrogen, nitrogen, and sulfur[7].

Table 1: Ultimate analysis of beech wood on a dry basis [7].

Ultimate Analysis (weight % on dry basis)	
Carbon	49.1
Hydrogen	5.7
Nitrogen	<0.3
Sulfur	0.05
Oxygen	44.5

Table 2: Proximate analysis for beech wood on a weight basis [7].

Proximate Analysis	
Moisture (weight %)	8.7
Volatile matter (weight % dry basis)	84.3
Fixed carbon (weight % dry basis)	15.2
Ash (550^{o}C) (weight % dry basis)	0.80
Ash (815^{o}C) (weight % dry basis)	0.46

Similarly, like the elemental analysis, biomass composition is based on cellulose, hemicellulose, and lignin, and the analysis of the fiber is given below[8].

Table 3: Fiber analysis for beech wood based on a dry basis [8].

Fiber Analysis (weight % on dry basis)	
Hemicellulose	37.1
Cellulose	41.7
Lignin	18.9

Cellulose and hemicellulose make up to 80% of the biomass, and lignin also contributes to 19% of biomass and contributes to product distribution also in the pyrolysis process.

3. Conversion Techniques:

Biomass is commonly used to produce bio-oil and there are several routes to convert biomass into different products using:

- Thermochemical Conversion.
- Biochemical Conversion.
- Physical Conversion.

A detail about the processes is given below:

3.1. Thermochemical Conversion:

Thermochemical conversion techniques for the conversion of biomass are the most extensively used and the most common processes are pyrolysis, liquefaction, and gasification. Combustion and torrefaction are also used for getting gaseous products and conditioning biomass for use in different processes.

3.1.1. Torrefaction:

Torrefaction is used to improve the properties of biomass and dry it at a certain temperature range to enhance the ability of biomass to be used for different processes. Different torrefactions can be achieved at different temperature ranges, with light torrefaction can be achieved between 200-235°C, mild torrefaction from 235-275°C, and severe torrefaction from 275-300°C. The typical product from the process includes CO, CO_2, CH_4, and H_2 in gaseous products while in liquid products there is water along with carboxylic acid and small amounts of ketones, aldehydes, and alcohols. This process is also a useful technique to reduce the oxygen content of the biomass making it more suitable for using it in other processes like pyrolysis the solid left after the process can be used as a treated coal with less amount of GHG and less environmental impact[8] [4]. A schematic for torrefaction is given below:

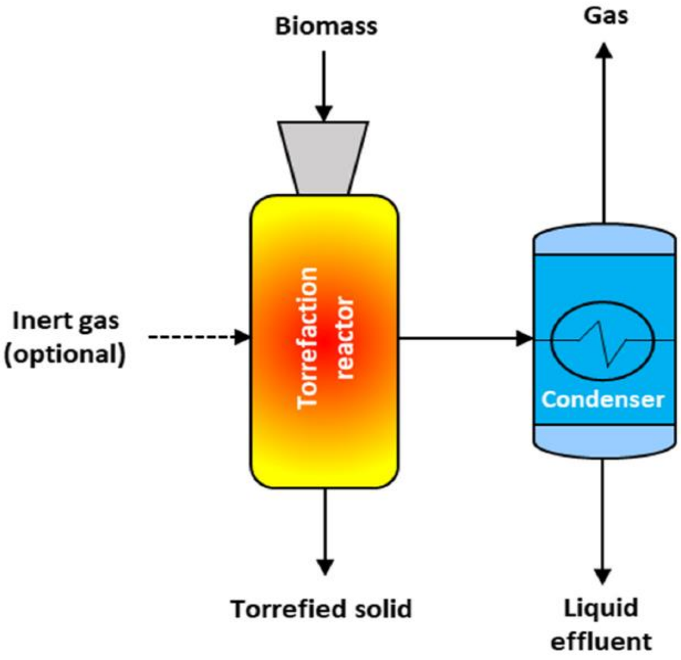


Figure 5: Torrefaction process using biomass as raw material [8].

3.1.2. Liquefaction:

Liquefaction is a process to convert biomass into crude bio-oil along with gaseous products. The process conditions are important for the product distribution, temperature in a range from 240-380°C and pressure 5-30 MPa is a suitable range for liquefaction. Having around 40% moisture in biomass, hydrothermal liquefaction (HTL) is a good technique to get products without drying biomass with extra energy giving it an advantage from the financial side. It converts undesired heteroatoms to CO_2, H_2O with oxygen, and with nitrogen, it converts to N_2 and N_2O, and inorganic acids with P elements[9] [10] [4]. Figure 6 explains the schematic for the liquefaction process.

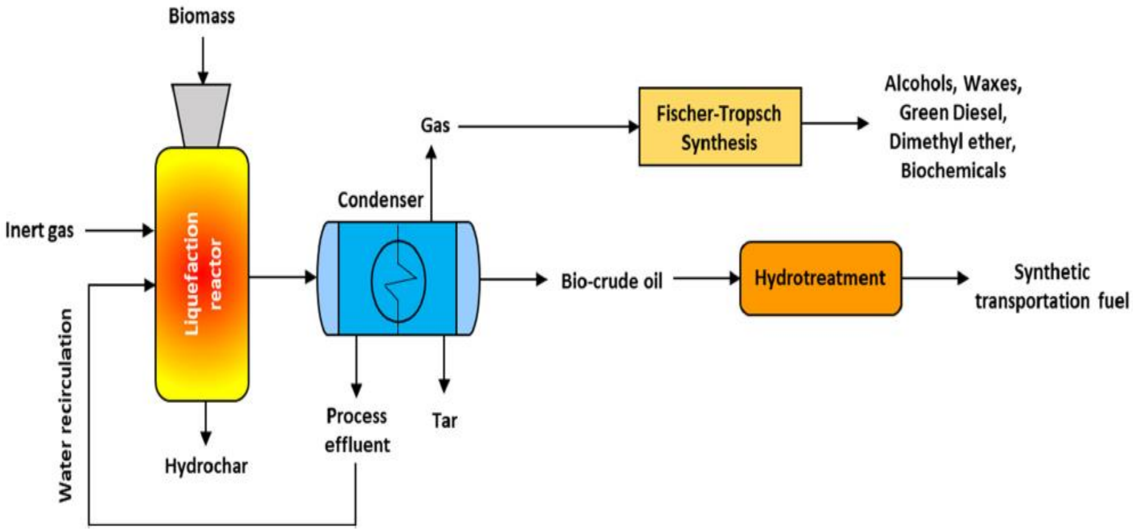


Figure 6: Liquefaction process with biomass and alternate routes for products fraction [8].

The gaseous and liquid products can also be converted to different commercial products using techniques mentioned in the flow diagram. The solvents like ethanol and subcritical water are used to breakdown the biomass and get products from it and these solvents are also recycled to be reused again in the process.

3.1.3. Gasification:

The production of syngas from biomass is done by the gasification process. It is also a thermochemical process that involves a reaction with biomass and either catalytic or non-catalytic depending on the process configuration. The temperature and pressure for catalytic gasification are 225-265°C and 2.9-5.6 MPa respectively. For non-catalytic conditions, the temperature is in the range of 800-1200°C. The biomass after drying goes to the pyrolysis process or partial combustion and then the gasification is done at a high temperature. The common gaseous composition obtained from the gasification process includes CO, H_2, CO_2, and CH_4. As high temperature favors gas phase reactions, products can be obtained by gasification process which can be used to get commercially viable fuels and other products with Fischer Tropsch synthesis[11] [12].

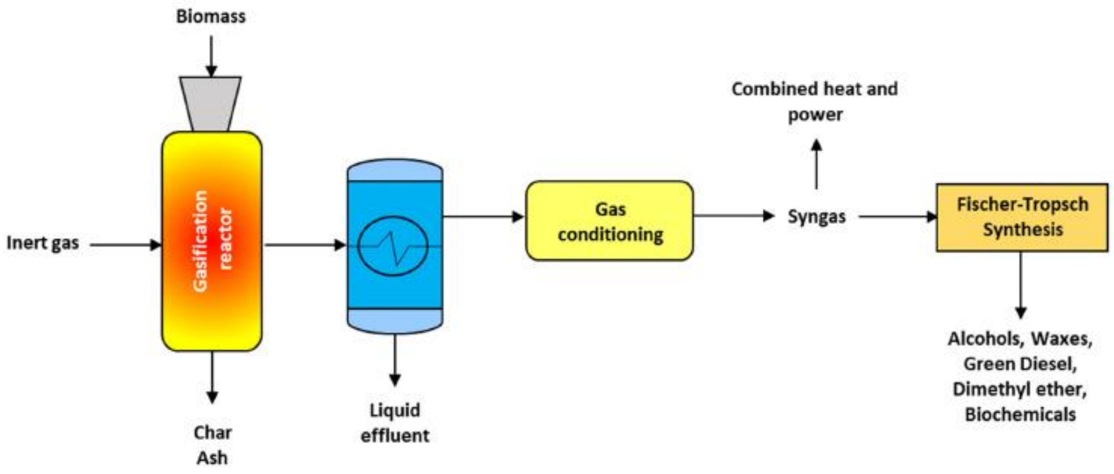


Figure 7: Gasification process using Fischer Tropsch for syngas treatment [8].

Hydrothermal gasification (HTG) can also be used like the HTL process to treat biomass for moisture content and then use it for the reactions to get products having high calorific value for syngas, high carbon conversion efficiency, and improved efficiency[13].

3.1.4. Pyrolysis:

The pyrolysis process can be done in different ways depending on the residence time of biomass in the pyrolysis reactor as it defines the product distribution. Temperature, pressure, and residence time play a critical role in defining product distribution. In slow pyrolysis, the main product obtained is char and other products are bio-oil and gases. The heating rate is around 0.1-1.0°C/s and the residence time is longer than other pyrolysis processes (> 30s). The fast pyrolysis is being done at a very high heating rate around >1000°C/s and the residence time is very less (<2s) with temperature ranges between 300-700°C. The difference between hydropyrolysis and fast pyrolysis is the process conditions are the same for both of the processes but in hydropyrolysis, hydrogen or water is used as fluidizing medium. The product distribution for both fast and hydropyrolysis are bio-oil along with gases and char in relative proportion as secondary products[12] [14] [15] [16].

The pyrolysis process should be done in the absence of oxygen as it leads to side reactions with the combustion of pyrolysis vapors being one and carbon yield can be lost there.

Table 4: pyrolysis process classification with product distribution [8].

Process	**Temperature (°C)**	**Heating rate (°C/min)**	**Vapors residence time**	**Bio-oil (wt%)**	**Biochar (wt%)**	**Gas (wt%)**
Slow	300-500	<50	>30 min	20-50	25-35	25-50
Intermediate	400-600	200-300	10 min	35-50	25-40	20-30
Fast/Flash	400-900	10-1000	<2s	60-75	10-25	10-30

A schematic for the pyrolysis process is shown in figure 8 and explains the process.

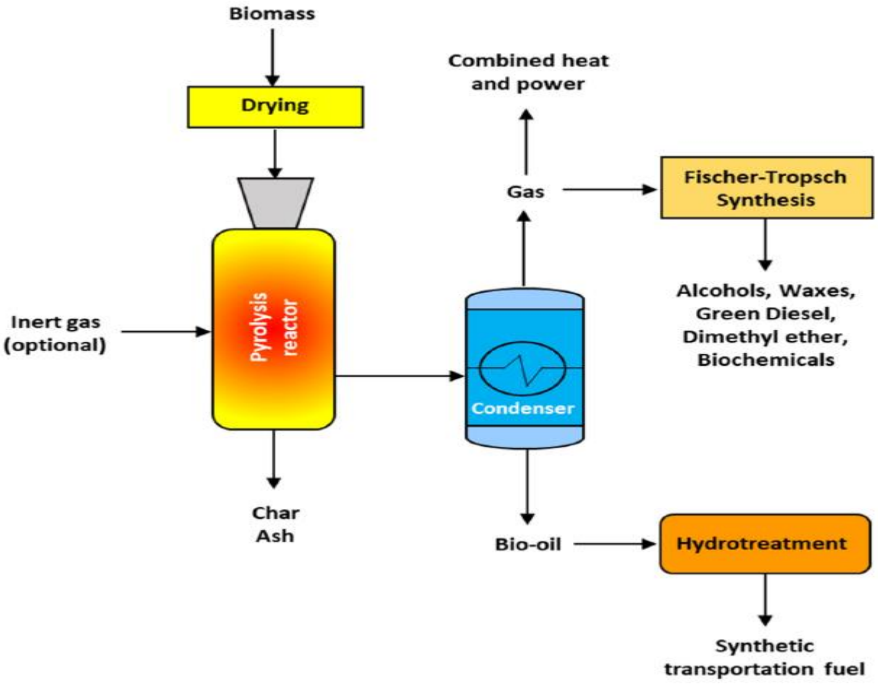


Figure 8: Biomass pyrolysis process with additional processes for fuel generation [8].

3.2. Biochemical Conversion:

Biochemical conversion of biomass involves the usage of microorganisms to convert biomass into useful products like biofuels and gases. This process can be achieved without specifying process conditions at ambient temperature and pressure. Microorganisms help in breaking down the complex biomass structure into simpler compounds. With anaerobic digestion, biogas primarily consist of methane and carbon dioxide produced and the process takes place in the absence of oxygen. Fermentation produces ethanol, hydrogen, and organic acids by breaking down complex carbohydrates into simpler sugar compounds and then into desired products. Enzymatic hydrolysis is also employed to break down cellulose and hemicellulose into sugars which can further be converted into products by fermentation and by other processes. Details about the biochemical processes can be studied in the reference paper[17] [18].

A schematic of biochemical conversion is shown in figure 9 with fermentation and digestion explained and the products from the respective process.

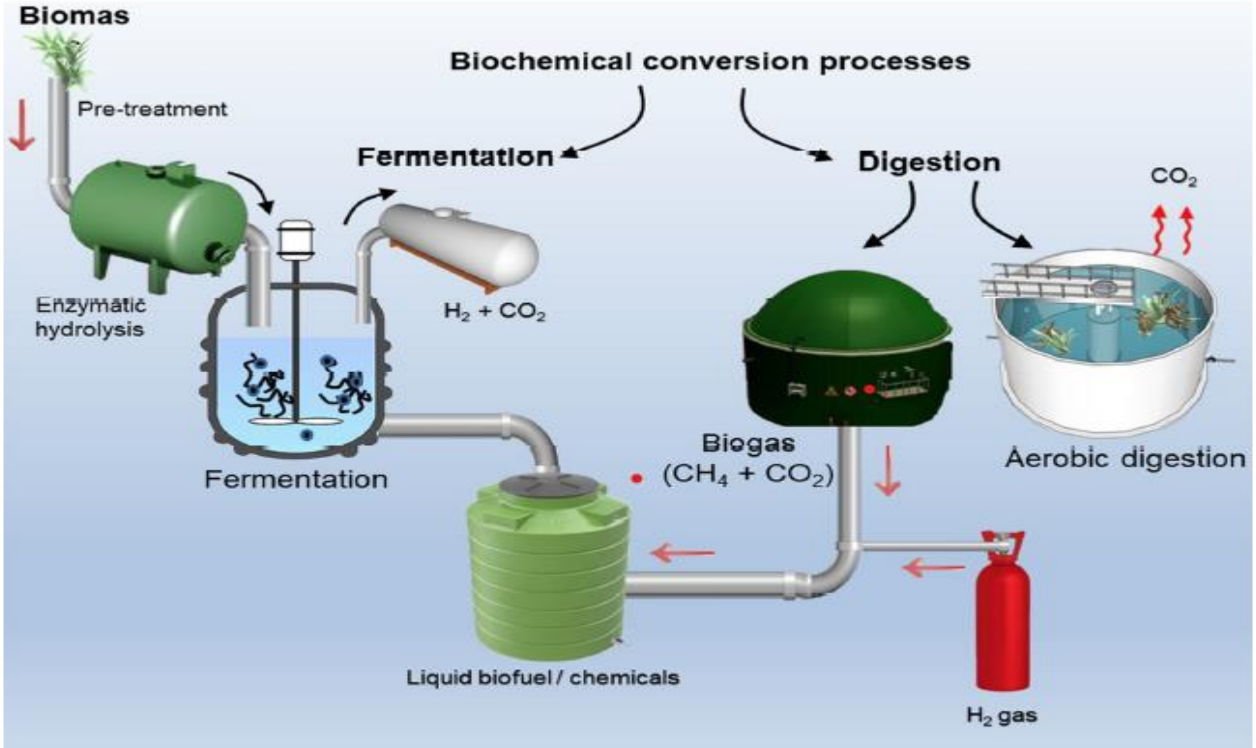


Figure 9: Conversion of biomass using biochemical conversion with alternate routes [17].

4. Hydropyrolysis:

Hydropyrolysis has got extensive attention in recent years to be used for the production of biofuels from biomass using the pyrolysis process route. It is a thermochemical process that involves the simultaneous application of heat, pressure, and hydrogen to convert biomass and or other carbonaceous materials to get bio-oil, gases, and solid residue(char). As coal needs hydrogen to produce hydrocarbon as a medium, hydropyrolysis resembles the Bergius process. The difference in both processes is that in the Bergius process, coal is mixed with heavy oil to have a slurry whereas in hydropyrolysis vapors phase reactions take place[19] [20] [21].

Having hydrogen in the pyrolysis process has many advantages over the conventional pyrolysis process. It restricts the formation of polyaromatics, olefins, and other compounds which are formed during conventional processes. The presence of hydrogen enhances the hydrogenation of intermediate compounds which can give a more suitable composition of bio-oil produced. Hetero atoms (oxygen) can be removed by breaking the complex molecules in biomass and increasing carbon yield without losing it with oxygen. It also facilitates the energy transfer to biomass and improves the overall energy efficiency of the process and less char formation also leads to higher oil yield[19] [20].

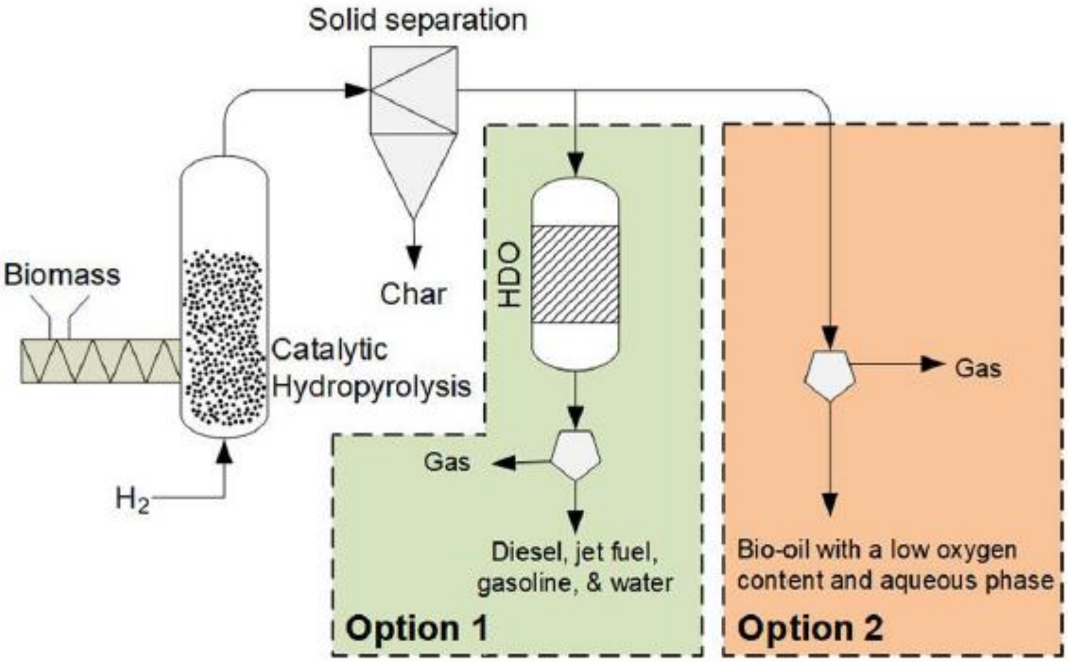


Figure 10: Hydropyrolysis process for biomass with HDO process for fuel production [20].

Hydropyrolysis can be coupled with different setups to obtain desired oil fractions. A simple process scheme is shown in Figure 10. It can be seen clearly that an additional process is also required to upgrade the bio-oil obtained from the hydropyrolysis process[20].

It is seen that hydrogen is passing through the bottom of the pyrolysis reactor in the hydropyrolysis process and nitrogen can be passed through during the conventional process. The upgrading can be done either by having a secondary reactor including upgrading catalysts or having hydro deoxidation (HDO) to get desired oil fractions[20].

4.1. Reactions in Hydropyrolysis:

The reactions in hydropyrolysis are somewhat similar to what occurs in conventional pyrolysis when biomass is decomposed upon heating giving pyrolysis vapors. In the presence of hydrogen, a set of additional reactions take place and with catalysts present ex-situ, the reactions are similar to hydrotreating and are explained below[22] [19].

Cracking: Reactions involving the breakage of bigger carbon chains in smaller chains resulting in the formation of smaller hydrocarbons[23].

$$\mathrm{C_{10}H_{22}} \longrightarrow \mathrm{C_8H_{18}} + \mathrm{C_2H_4}$$

Hydrocracking: Similar reactions like cracking but in the presence of hydrogen to give smaller hydrocarbons[23].

$$\text{heavy hydrocarbon} + \mathrm{nH_2} \longrightarrow \text{light hydrocarbons}$$

Decarbonylation: Removal of the carbonyl group (-C=O) from the compounds is a significant reaction for the removal of oxygen from bio-oil obtained during pyrolysis. Removal of the carbonyl group gives away CO and hydrocarbon with the addition of hydrogen atoms [20].

$$\mathrm{RCHO} \longrightarrow \mathrm{RH} + \mathrm{CO}$$

Decarboxylation: Removal of a carboxyl group (-COOH) resulting in the release of CO_2 and formation of hydrocarbons from compounds vapors from hydropyrolysis from lignocellulosic components of biomass[20].

$$\mathrm{RCOOH} \longrightarrow \mathrm{RH} + \mathrm{CO_2}$$

Hydro-deoxidation: It is an important reaction to reduce oxygen from functional groups containing oxygen like hydroxyl (-OH), carboxyl (-COOH), and carbonyl group (-C=O) with hydrogen to reduce the compounds giving away hydrocarbons. The direct deoxidation (DDO) pathway is a reaction pathway in which oxygen is removed directly without any intermediates formed in a single step[24].

$$\mathrm{R - OH} \longrightarrow \mathrm{R - H + H_2O}$$

Hydrogenation: It occurs simultaneously with the thermal decomposition of biomass in the presence of hydrogen to convert unsaturated biomass-derived compounds into more saturated compounds. Hydrogen is also supplied externally in hydropyrolysis for enhanced hydrogenation throughout the process[20].

$$\mathrm{RCH = CH_2 + H_2} \longrightarrow \mathrm{RCH_2 - CH_3}$$

Alkylation: It is the reaction between compounds particularly aromatics along with pyrolysis intermediate compounds like phenols, acids, and alcohols to produce alkylated hydrocarbons and can have bigger chain-length compounds by alkylation. It should be controlled as alkylation can produce bigger hydrocarbon which can hinder downstream processing of oil[25].

$$\mathrm{R-CO-R' + RX \dashrightarrow\; R-CO-R'R'' + HX}$$

4.2. Mechanistic model for hydropyrolysis:

The mechanistic model explains the conversion of biomass to different products following the reaction's mechanism. In conventional fast pyrolysis, biomass goes to primary char along with gases and liquid metaplast. The metaplast then goes to secondary char following up the cracking reaction. With catalysts in catalytic hydropyrolysis, the biomass can be converted to the same products as in the conventional process with additional reactions to convert the products to a more stable form as the products obtained from the conventional process can be questioned to stability. The changes were observed in the presence of catalysts and the addition of hydrogen[20] [19]. Dayton et. al. and Meesuk et. al. observed a considerable decrease in yield for char along with other product distribution when the medium changed from nitrogen to hydrogen. Along with that Dayton, et. al. stated that using hydrogen can increase the yield for liquid products and Meesuk et. al. mentioned that gas yield increases by using hydrogen as a medium. Both statements can be justified by taking into consideration that temperature difference plays a role in product distribution as Dayton et. al. has 400^{o}C in the system and Meesuk et. al. has 600^{o}C in the system[26] [27].

Figures 11 and 12 explain the pathway for the decomposition of biomass into different products both for the conventional pyrolysis process and the hydropyrolysis process. It can be noted that with additional reactions in hydropyrolysis, desired products can be obtained with commercial value.

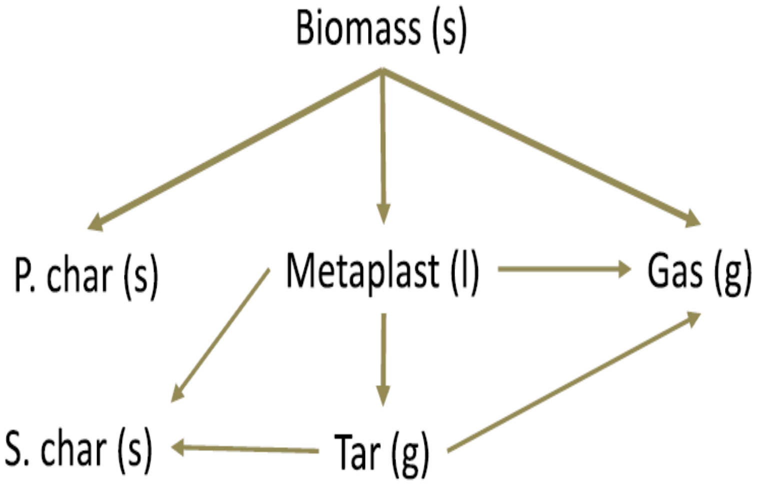


Figure 11: Biomass decomposition in conventional pyrolysis process [20].

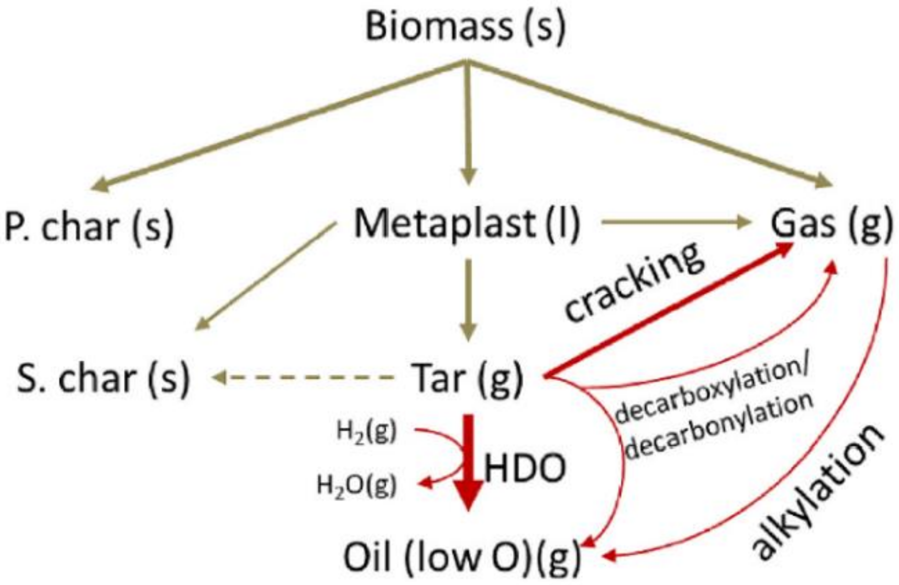


Figure 12: Biomass decomposition with pyrolysis under catalytic activity [20].

A schematic for fast pyrolysis, hydropyrolysis, and catalytic hydropyrolysis can be seen in figure 13 with two raw materials studied, and the pathway is developed in a microreactor study. It can be noted that DE% (degree of extent of pyrolysis) and HLE% (hydrogen loss extent) are more in catalytic hydropyrolysis as compared to non-catalytic hydropyrolysis and fast pyrolysis routes. The reactions are almost similar in three paths with additional reactions in the catalytic pathway[28].

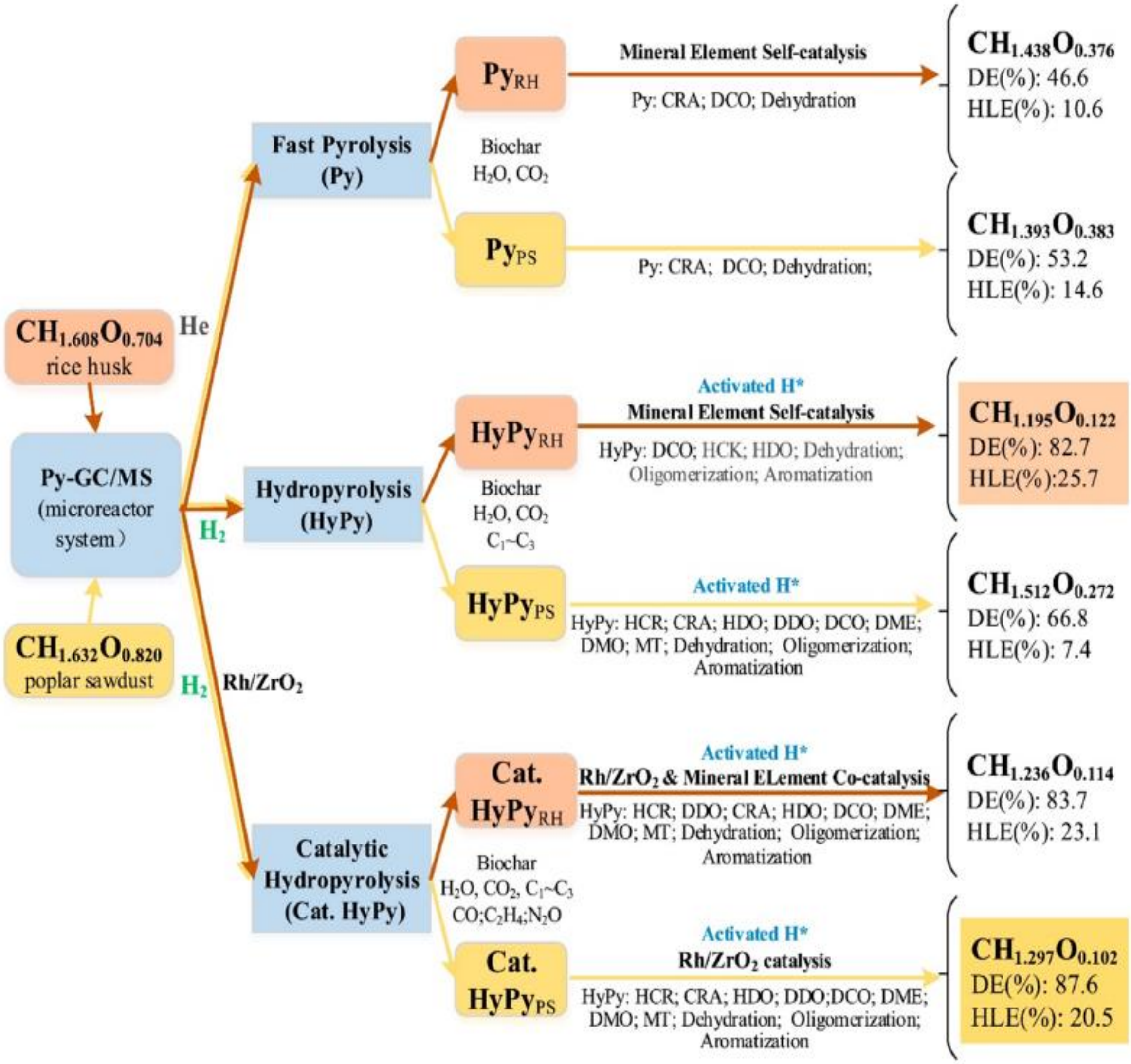


Figure 13: Comparison between pyrolysis processes with catalytic activities [28].

4.3. IH_2 Technology:

IH_2 technology, integrated hydropyrolysis and hydro conversion combined was developed by GTI organization and acquired by Shell. It can be used to convert biomass feedstock into gasoline/diesel products which can be a direct substitute for fossil fuels. This technology couples two processes and has several advantages, biomass treatment is the first step and the pressure conditions are around 20-35 bar. The flue gas separation from fuel produced occurs after the hydrotreater unit. Hydrogen produced can be used as a fuel by burning gases (C_1-C_3) as it can eliminate the use of external hydrogen supply. The oxygen content was also removed thermo-catalytically from the feed in the form of water and CO_x, the coking on the catalysts was reduced and the lifetime also increases for the catalysts by catalytic hydropyrolysis reactions. Liquid yield ranges from 25-30% with molar hydrogen to carbon ratio ranging from 1.4 for biomass and 1.7 for algae[29] [30]. The process diagram in Figure 14 shows the IH_2 plant.

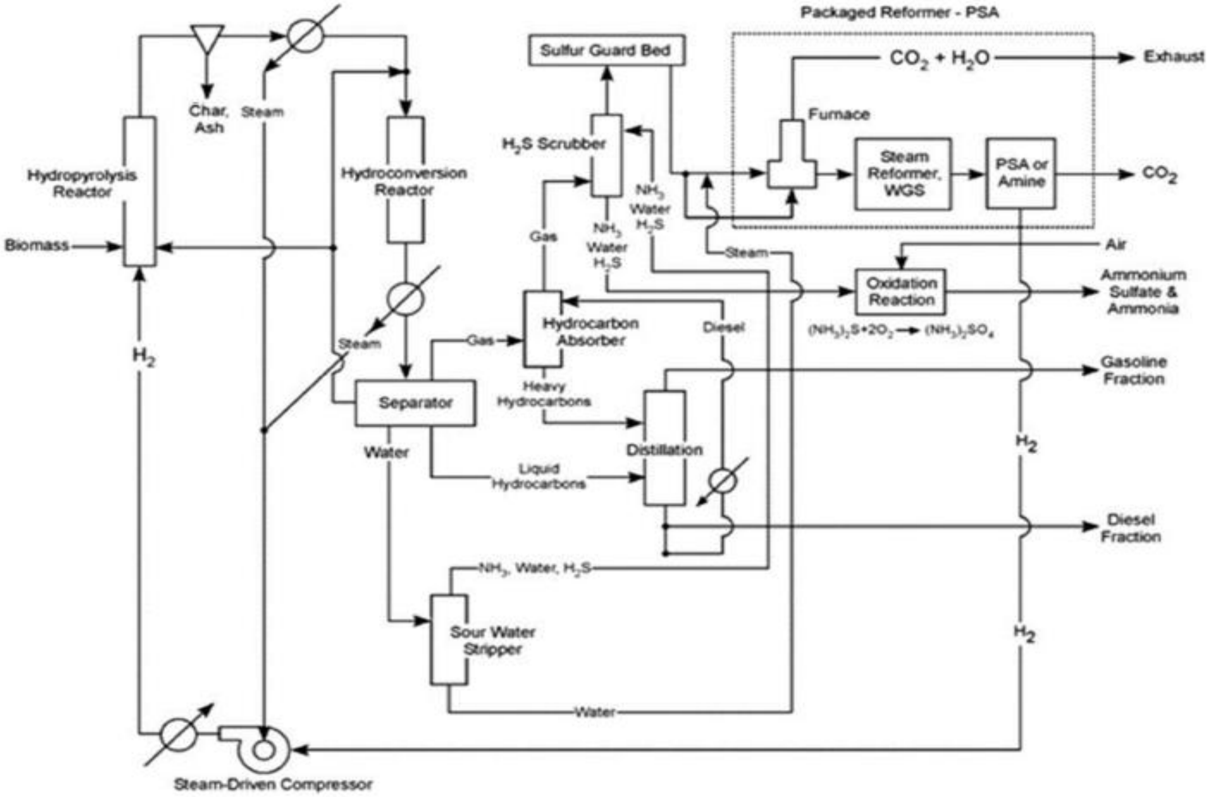


Figure 14: IH_2 process flow diagram [29].

4.4. Other Technologies:

Other technologies have similar processes with different working conditions are explained below:

4.4.1. H_2 bio-oil process:

In this process, hydrogen is supplied in the first reactor separately for the hydropyrolysis process, and in the secondary reactor, an HDO catalyst is used to get the bio-oil[31].

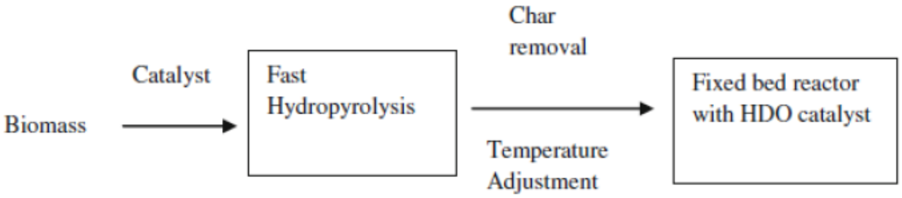


Figure 15: H_2 bio-oil process [31].

4.4.2. H_2 bio-oil-C process:

In this process, integration gasification combined cycle (IGCC) along with the H_2 bio-oil process, hydrogen provided by syngas is produced in the coal gasifier while in the previous process, hydrogen is supplied separately with an external source. This process has several advantages, low capital and maintenance cost, and no requirement for sand as a heating medium. The gases and char produced can also be used in coal gasifiers and gas turbines [31].

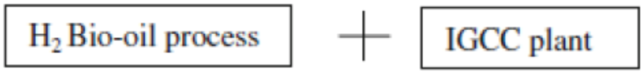


Figure 16: H_2 bio-oil-C process [31].

4.4.3. H_2 bio-oil-NG process:

The difference between this process and the H_2 bio-oil-C process is that a steam methane reformer (SMR) is used instead of a coal gasifier in this process and SMR gases are used for hydrogen and heat. It is a cost-effective process and heats to SMR can be provided by HDO and hydropyrolysis reactor[31].

Figure 17: H_2 bio-oil-NG process [31].

4.4.4. H_2 bio-oil-B process:

The gasification process is combined in this setup to provide hydrogen to the H_2 bio-oil process, and the sequence to provide for hydropyrolysis and HDO reactor. In this process, water gas shift (WGS) reactions can reduce the external supply of hydrogen along with catalysts present[31].

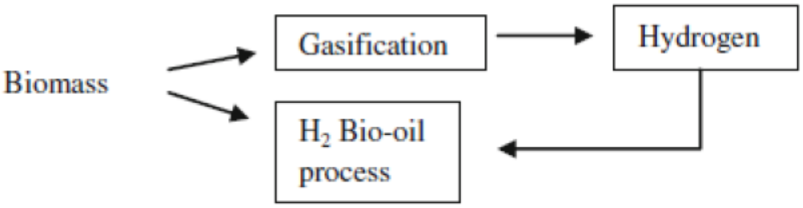


Figure 18: H_2 bio-oil-B process [31].

4.5. Reactors Used in Hydropyrolysis:

The progress made in hydropyrolysis and the positive impact of the process in comparison to the conventional pyrolysis process, different classifications have been under study with different heating gases like hydrogen and nitrogen and fluidizing medium also like sand, dolomite and or catalysts (primarily FCC) in the pyrolysis reactor. Dutta et. al. studied the classifications with different arrangements and places of upgrading catalysts. The most prominent arrangements are explained below as can be seen in Figure 19. These arrangements were also studied by other research groups along with different configurations[32] [33].

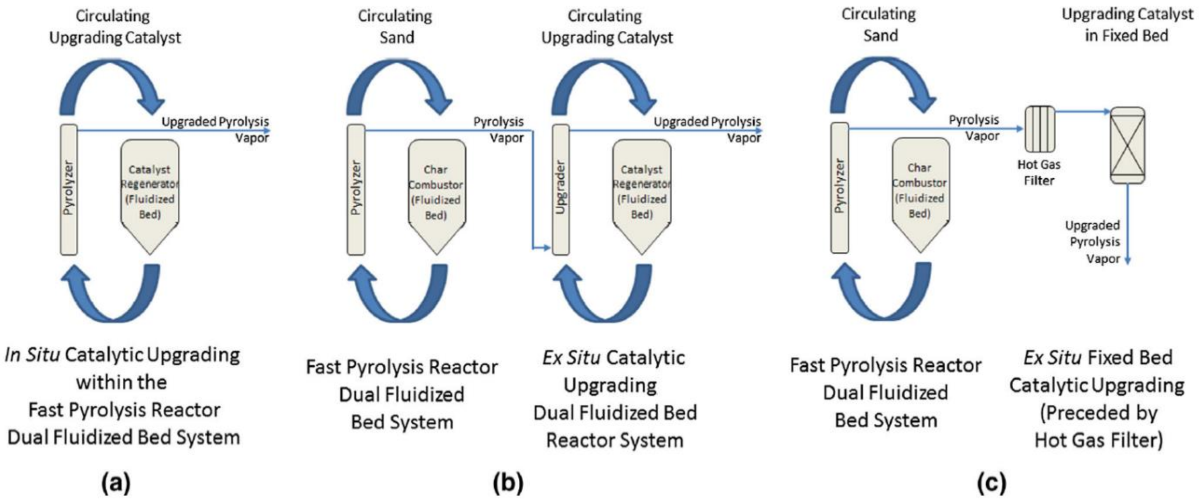


Figure 19: Different arrangements for catalytic upgrading in pyrolysis process [32].

In arrangement (a) a single reactor is used for pyrolysis and upgrading with catalysts in situ. In (b) the upgrading catalysts are ex-situ but in a fluidized bed system. For both arrangements, catalysts regeneration is quick but is prone to loss and attrition. Ex situ catalysts are focused in a fixed bed reactor arrangement and different catalysts are also being developed for vapors upgrading. Arrangement (c) is also in the same analogy as having ex-situ fixed bed reactor holding catalysts for upgrading. Hot gas filter upstream of ex-situ reactor to remove particulate materials passing through a cyclone separator. It will prevent particulates from going to catalysts and hindering catalytic activity and alkali-containing minerals also be removed[32] [33].

Having hot filters, carbon loss is around 10% from biomass feedstock in the form of coke and non-condensable light gases like CO, CO_2, CH_4, and C_2H_4. The 10% loss is documented based on resulted in literature. In the general process scheme, cyclone separators are used for removing char and particulates present in the stream without having hot gas filters, still, it can be used according to the arrangement and process requirements. The C-C coupling reactions are thermodynamically limited with narrow ranges for product distribution. Reduced coking, oxygen content, and catalyst flexibility are noted in ex-situ configuration[32] [33].

Anker et. al. studied arrangements for hydropyrolysis with the possibility of having ex-situ reactors with catalysts and the effect on product distribution. Two arrangements with a single reactor having inert and catalytic medium and two with double reactors with inert and catalytic medium[34] [35].

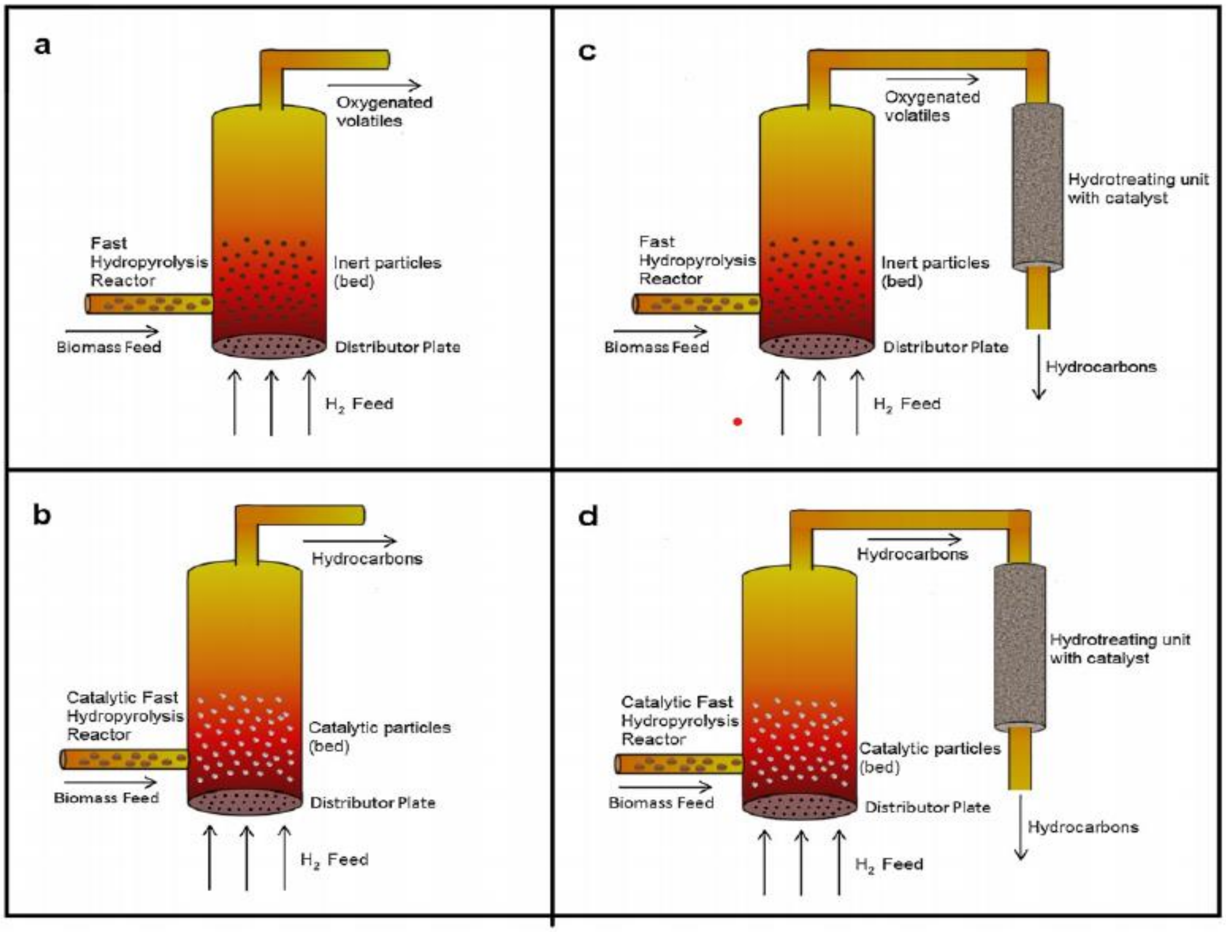


Figure 20: Upgrading schemes with inert and hydropyrolysis process [35].

In a single-stage configuration, the continuous circulation of catalysts causes loss due to attrition. Phenolic hydrocarbons increase and deoxygenation of large phenolic compounds to phenols and then to aromatics. Lignin hydrogenolysis increases H_2 pressure and form gases like CO, CO_2, CH_4, C_2H_4, and C_2H_6. It is interesting to note that the product distribution remained unchanged but aromatic hydrocarbons increased in the presence of catalysts for a single-stage reactor[35].

The reactions in hydropyrolysis have several pathways and the coking of catalysts have been reduced as compared to conventional pyrolysis. In this regard, zeolites are prominent in industrial operations for increased carbon recovery. HZSM-5 notably increases hydrocarbons and decreases CO_2, and it also helps in upgrading bio-oil with a reduction in coking for the catalysts.

With two-stage reactors, the oxygen content of the bio-oil can be reduced, and it can be made viable for direct replacement of fossil fuels. Energy consumption is a big concern in hydrotreating units and direct conversion of pyrolysis vapors can be utilized for it. Before, a two-stage arrangement was tested for hydropyrolysis of coal, and reduced heteroatoms were noted in the final bio-oil so having catalysts in the hydrotreating unit will have an advantage in upgrading bio-oil. As in IH_2 technology, hydropyrolysis suppresses polymerization reactions, but the oxygen content is removed by HDO reactions in an ex-situ reactor and oxygen content is removed majorly in two-stage arrangements[36][26] [37].

Biomass cracking can affect catalyst's activity and they are prone to coking so catalysts are always placed in a secondary reactor. Also, the regeneration of catalysts can be done easily in the second reactor and energy consumption is also reduced in it. Greenhouse gases (GHG) are also reduced with IH_2 technology in comparison to fossil fuel production[35].

4.6. Bio-oil Upgrading:

The need for bio-oil upgrading is important to have it suitable for using it in place of fossil fuels and making it suitable in parameters like viscosity, oxygen content, carbon range, and water content as bio-oil from biomass has a large amount of oxygen in raw bio-oil which can’t be used directly. Table 5 gives a comparison between pyrolysis bio-oil and heavy petroleum oil[10].

Table 5: Bio-oil and heavy petroleum oil properties comparison [10].

Properties	Bio-oil	Heavy petroleum oil
pH	3.8-4.0	-
Acid value (mgKOH/g)	1.8	-
Density (g/cm^3)	1150-1200 at 40°C	940
Viscosity (cP)	650 at 40°C	180 at 40°C
HHV (MJ/kg)	28.42	40
C (wt.%)	66	85
H (wt.%)	11	11
O (wt.%)	12	1.0
N (wt.%)	9	0.3
S (wt.%)	1	-
Water content (wt.%)	12-13	0.1
Ash content (wt.%)	0.4-0.7	0.1

As bio-oil is a complex mixture of aromatic compounds along with phenolic derivatives and oxygenated compounds and the distribution changes with raw material and process conditions and thermochemical processes. In comparison, water and oxygen content is high in petroleum oil, and HHV is also less for bio-oil. The pH is also in the corrosive range because of the presence of fatty acids in bio-oil, high viscosity with side reactions having polymerization as a part of it increases the viscosity of bio-oil and upgrading is necessary for it[38] [39].

There are several methods possible to upgrade bio-oil with pros and cons of every method and limitations. Hydrotreating removes heteroatoms from bio-oil along with sulfur, but catalysts deactivation and pressure requirements are important for the process. Also, having high-temperature resistive equipment for commercial scale should be considered. Catalytic cracking and reforming processes also need high temperatures for reactions in the presence of catalysts.

Separating valuable chemicals from bio-oil can be done by extraction, an expensive process and still needed to find an economical alternative for it. Having hydrogen in the system affects coke formation but the product distribution also changes as compared to inert atmosphere[40] [39].

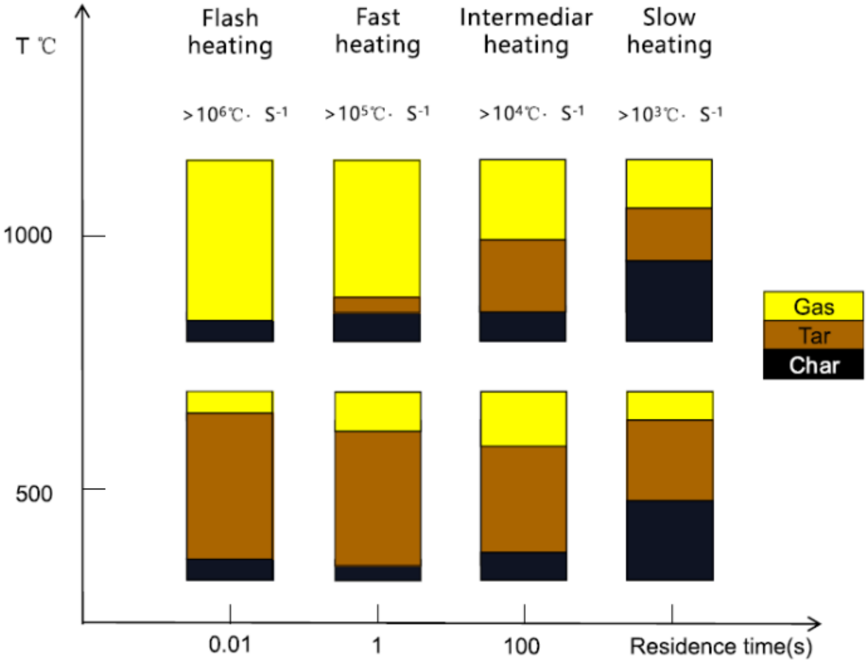
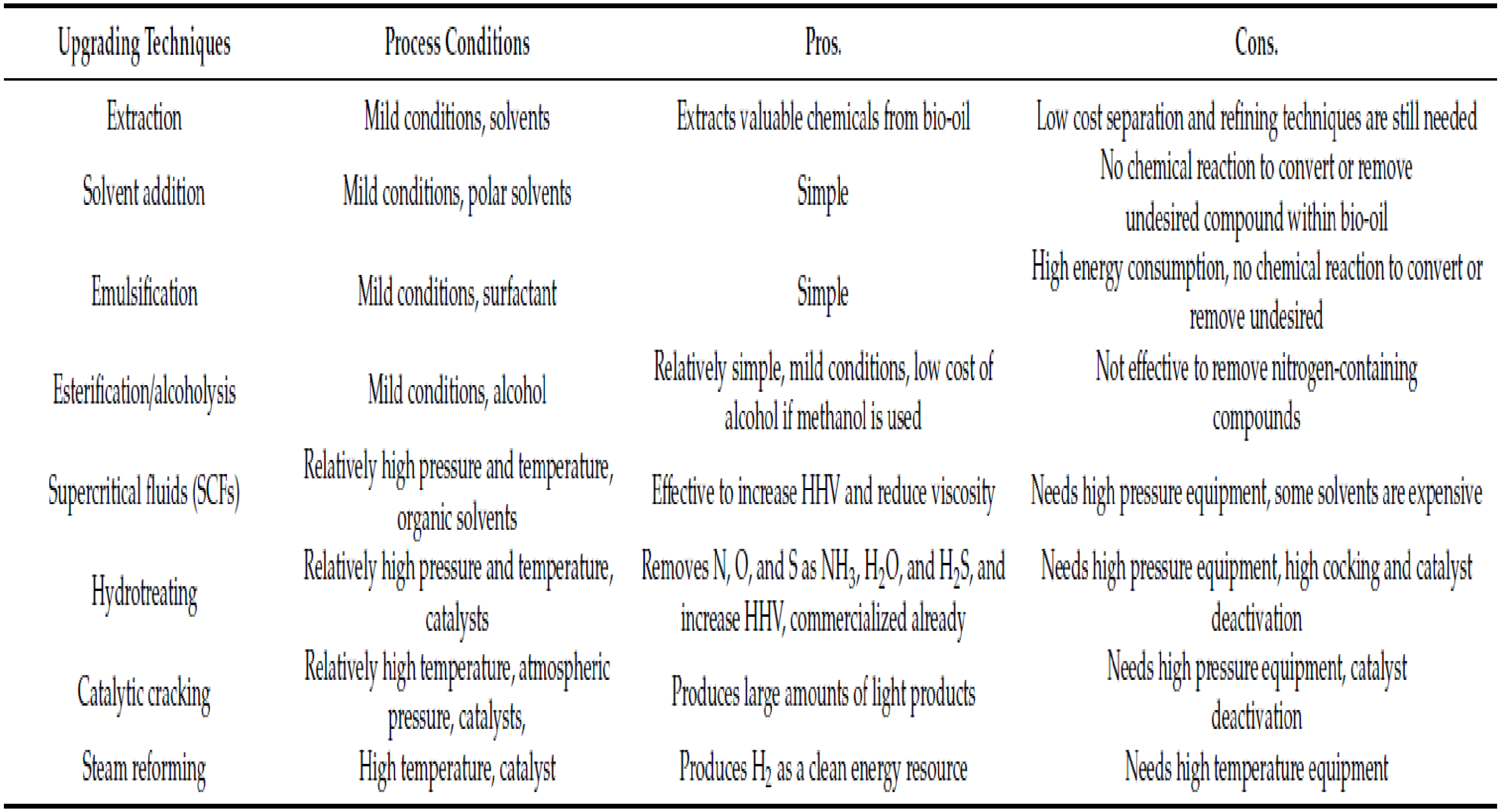


Figure 21: Product distribution as a function of residence time [40].

With catalysts taking part in the reactions, desired product distribution can be obtained, and activation energy is also reduced. The catalysts are zeolites including ZSM-5, titanium dioxide-based, and alumina-based catalysts has shown prominent results in the upgradation process. And the financial aspect of capital cost and having noble metals catalysts have a big impact on the implication of the process. Cost reduction in terms of energy reduction from pretreatment of biomass to remove moisture and size reduction also should be considered[39].



Upgrading Techniques	Process Conditions	Pros.	Cons.
Extraction	Mild conditions, solvents	Extracts valuable chemicals from bio-oil	Low cost separation and refining techniques are still needed
Solvent addition	Mild conditions, polar solvents	Simple	No chemical reaction to convert or remove undesired compound within bio-oil
Emulsification	Mild conditions, surfactant	Simple	High energy consumption, no chemical reaction to convert or remove undesired
Esterification/alcoholysis	Mild conditions, alcohol	Relatively simple, mild conditions, low cost of alcohol if methanol is used	Not effective to remove nitrogen-containing compounds
Supercritical fluids (SCFs)	Relatively high pressure and temperature, organic solvents	Effective to increase HHV and reduce viscosity	Needs high pressure equipment, some solvents are expensive
Hydrotreating	Relatively high pressure and temperature, catalysts	Removes N, O, and S as NH_3, H_2O, and H_2S, and increase HHV, commercialized already	Needs high pressure equipment, high cocking and catalyst deactivation
Catalytic cracking	Relatively high temperature, atmospheric pressure, catalysts,	Produces large amounts of light products	Needs high pressure equipment, catalyst deactivation
Steam reforming	High temperature, catalyst	Produces H_2 as a clean energy resource	Needs high temperature equipment

Figure 22: Upgrading techniques for crude bio-oil [39].

4.7. Parameters affecting Pyrolysis:

The process conditions are important in pyrolysis as distributions can change a lot both in conventional and hydropyrolysis. The most important parameters are temperature, pressure, heating rate, residence time, and catalysts for the catalytic pyrolysis process.

4.7.1. Pressure:

Pressure is important in the pyrolysis process as the final product distribution changes a lot and certain reactions get started under the influence of pressure. In hydropyrolysis, having high hydrogen pressure generates more gases and lighter non-condensable hydrocarbons but the amount of oxygen decreases considerably. Bio-oil quality improved with the presence of hydrogen and additional chemical reactions occur in hydrogen so increasing hydrogen should be done with great monitoring and should be regulated for a certain limit to have a desirable product distribution. Hydrodeoxygenation is favored at high pressure for hydrogen and hydropyrolysis efficiency increases with pressure increased[41] [42].

4.7.2. Temperature:

The effect of temperature is very important for carrying out pyrolysis and the influence is very high for product distribution. Several research groups documented the importance of temperature and increasing temperature for catalytic pyrolysis can reduce oxygen content to around 50% in certain raw materials. Increasing too much temperature can lead to cracking reactions and increase gases in the product distribution with less amount of bio-oil produced. Elliot et. al. studied the effect of increasing temperature on wood-derived bio-oil with Pd/C catalyst and found that the increase in temperature from 310^{o}C to 360^{o}C reduced the bio-oil yield from 75 to 56% and reduced the deoxygenation process from 65 to 52% with an increase in gases. The reactivity of individual species changes with temperature and it also changes the distribution for the final products.

Phenolics are completely converted to aromatics with increased process temperature but thermodynamic limitation in hydropyrolysis should also be taken under consideration. At low temperatures, the bio-oil produced contains primarily alkanes, alkenes, long-chain fatty acids, and esters. With high temperatures, alcohols, ketones, and aromatics are obtained. Gas yield also increased with it and coking on catalyst also increases[42] [43].

4.7.3. Particle Size:

The reduction of particle size is important in the pyrolysis process to have a good degree of initial reactions that occur on biomass particles. Biomass in general is not a good conductor of heat and this can hinder the activity of breaking down biomass particles in pyrolizers to have a good extent of reactions. It should not be too to support gas phase reactions as having too small particles would lead to more gases in the products and less bio-oil[36] [26].

Shen et. al. studied bio-oil yield in comparison to biomass particles and results showed 12-14% more yield obtained with biomass particles around 0.3mm than particles with 1.5mm of biomass particles. Abnisa et. al. reported that particle size does not play any part in bio-oil distribution but in general analogy, it is noted that having fine particles can increase bio-oil yield with good heat transfer but too fine can increase gases also[44].

4.7.4. Residence Time:

Residence time is also an important factor as it classifies the type of pyrolysis process occurring and it is important to have good heat transfer during that time for biomass particles. The product distribution is different for different pyrolysis processes with residence time differences. Fast pyrolysis, having a residence time of <2s gives bio-oil as the main product and vapors should be removed quickly as secondary reactions would start decreasing bio-oil yield with an increased amount of char and gases. Repolymerization upon thermal cracking of pyrolysis vapors decreases bio-oil yield[21] [45].

4.7.5. Other factors:

Several other factors also affect product distribution and bio-oil production during the process. Factors including feeding rate, flow rates, and catalysts loading are important to note. Low feeding rates can have higher heat transfer in biomass particles and quick devolatilization, but it also increases gases in the products. Having a high feeding rate avoids cracking reactions and secondary reactions but heat transfer should also be considered[22].

Fluidizing gases like H_2 and N_2 are important for heat transfer and volatiles throughout the plant. Kim et. al. noted that sweeping gases in the system influence the heating rate, temperature, and secondary reactions of volatiles. It is also noted that for a fixed bed reactor nitrogen flow of 150-200 mL/min gives a maximum yield of bio-oil with limitations to increasing more gas flow through the system[22].

5. Resources:

The equipment for the analysis, pilot plant for experimentation, catalysts, and chemicals used along with catalysts are listed below:

5.1. Gas Chromatography:

Gas chromatography (GC) is used to analyze bio-oil samples and gases produced during experiments. Both gas and liquid samples were analyzed on separate equipment, gases were analyzed online during experiments whereas liquid samples were analyzed offline. Inert gas is used as a carrier for transporting samples to the column where samples get volatilized and chemical compounds in the samples with different classes are carried to the detector with carrier gas like N_2. Specific compounds are detected with their specific volatility and mass while interacting with the walls of the column. The column is of stainless steel and silicate glass having alkaline nature.

For gas samples, GC FID/TCD was for the detection of light hydrocarbons along with CO, CO_2, H_2, and N_2. A thermal conductivity detector (TCD) is a concentration-sensitive detector that works based on the difference in thermal conductivity of the carrier gas and the sample. The sample range is 10^{-6} to 10^{-8} gm per peak and the linear range is 10^{-4}. The sensing material can be a heated metal wire or a thermistor as well and the heat loss from the sensor while the carrier gas is flowing with the sample and when it enters the chamber the thermal conductivity changes with temperature difference generating a signal proportional to the concentration of the vapors in sensor cavity.

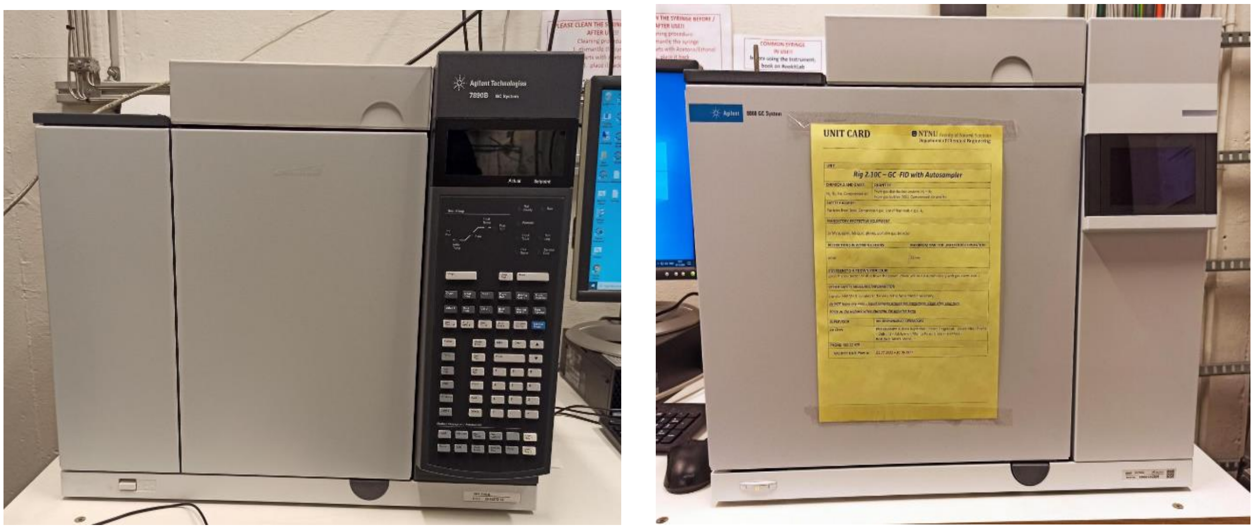


Figure 23: GC TCD/FID for samples analysis.

For liquid samples, GC FID is used. A flame ionization detector (FID) works by detecting an increase in electrical conductivity when the sample is broken down into ions with the help of hydrogen burning. There is a proportional relationship between ions generated and concentration and electrical signal. The main focus is on detecting hydrocarbons in the range C_2-C_6, nicotine, and related alkaloids. As all organic compounds give response, having specific compounds detected is not easy and water and non-condensable gases like CO and CO_2 are not detectable.

GC-MS is used to analyze liquid samples to identify compound spectra with specific retention times. Samples injected into the analyzer elude and gives spectra of respective compounds at specific times with ion chromatograms. It helps identify compounds present in bio-oil samples as bio-oil samples have more than a hundred compounds and having retention times of specific compounds would be easy for future use of the library in GC FID for analysis.

5.2. Karl Fischer Titration:

Karl Fischer titration is used to identify the percentage of water in liquid samples like bio-oil and other organic compounds. The purpose is to identify the percentage of water produced during the pyrolysis process as it can undermine the quality of the main product and should be separated. The titration principle is based on the oxidation of sulfur dioxide by iodine with water consumed in a buffer solution. The reaction between water, sulfur dioxide, and iodine is:

$$I_2 + 2H_2O \dashrightarrow 2HI + H_2SO_4$$

Water and iodine both react in equal amounts and the titration finishes when a titrating agent gets equal to the volume then it reacts with water in the sample. The reaction is pH sensitive, so buffer solutions should be used for acidic or basic samples for analysis[46].

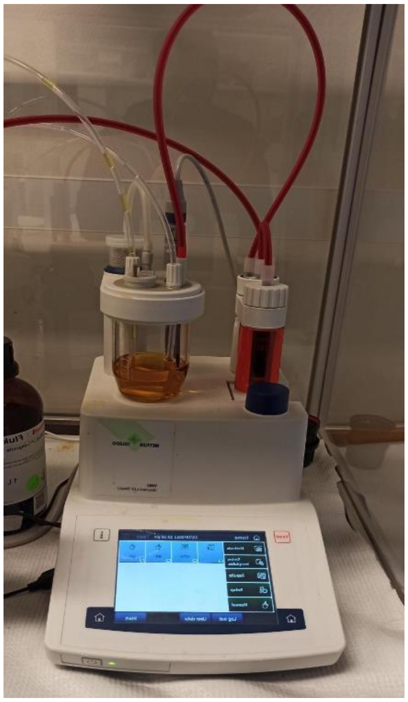


Figure 24: KF titrator for aqueous phase samples.

KF titration has two primary methods naming volumetric and coulometric and a new hybrid KF method has also been in use. Both methods are combined for the new method and a measured amount of iodine is added with water.

5.3. Rotary Evaporator:

A rotary evaporator is used for removing solvents form liquid samples obtained after cleaning the condensers giving off bio-oil after evaporation. It is a good equipment to separate chemicals with different boiling points and reused them for the same purpose. Acetone is used for cleaning up the condensers after experimentation so it can be reused after separating with the help of a rotary evaporator.

Figure 25: Rotary evaporator setup for bio-oil separation.

It has a vacuum source to have a vacuum inside the distillation column to boil out the solvent quicker. A mechanical pump attached to the distillation column creates a vacuum and condensation of vapors is done with the help of cooling water supplied to the column inside the spirals of the column. The round bottom flask attached to the right side of the column is for samples with acetone and residual bio-oil. A collection flask is attached at the bottom of the column to collect acetone which is separated and condensed back. The water bath is also used to heat up and vaporize the sample and it can also be rotated at a set speed, also the temperature of the water bath is adjusted according to the solvent to separate from the sample.

5.4. Chemicals:

There are several chemicals used as solvents during experiments and for cleaning the rig after experiments. Primarily acetone is used for cleaning the rig and to wash out bio-oil samples, ethanol is used for KF titration to dilute the bio-oil samples and GVL is used as a solvent to trap compounds leaving condensers without condensing and going out. GVL bottle is attached after the condensers just before the gas line which is going towards GC FID/TID for gas sampling.

5.5. Catalysts:

Catalysts used in the upgrading process for hydropyrolysis play an important role in the quality of upgraded bio-oil. Catalysts used have different abilities with associated reactions mechanism. Several catalysts have been studied primarily zeolites including Y-zeolite, HZSM-5, and titanium dioxide and alumina-based catalysts with reduced transition metals for activity. C-C coupling catalysts and hydrodeoxygenation catalysts are of more importance, to remove oxygen from compounds and give off hydrocarbons.

5.5.1. Metal oxides:

Several metal oxides can be used as catalysts directly providing certain advantages to the process or can be used as a support for active metals to hold for reactions. Alumina, titanium dioxide, and silica are the most commonly used catalyst supports.

Alumina (Al_2O_3) is used enormously as catalyst support in the pyrolysis process, and it has a strong ability to dehydrate with a higher surface area and strong acid sites for it. It has mechanical and thermal stability providing a large number of active sites for the metals and reactants. However, it is prone to coking because of the carbonaceous intermediates forms by pyrolysis vapors getting in contact with the vapors. Pt/Al_2O_3 is one example of having alumina as a support for the catalyst as platinum is a very good oxidizing agent and has shown great results within pyrolysis process reactions for upgrading bio-oil[47] [48].

Figure 26: Fresh (left) and spent (right) catalyst prepared inhouse.

Titanium dioxide (TiO_2) is being used as catalyst support very commonly as it has many advantages over other oxides. It has excellent thermal stability and can be used for high-temperature processes giving resistance to them. It has high acidic and basic properties that makes it suitable for both type of reactions and the chemical inertness of TiO_2 makes it more suitable to be used as it avoids side reactions to form intermediates. Pure titanium dioxide can easily be covered up with coke, reducing it before impregnating metals gives advantages with increased stability, catalyst-support interaction, and increased surface area for good metals contact with the support and also effective with deoxygenation and cracking reactions. It also has active sites for reactions and is used as a catalyst itself with strong hydrogenation ability[49] [50].

5.5.2. Transition metals:

Transition metals are widely used for catalyst preparation with their ability to take part in reactions directly without going to side reactions. They have good hydrogenation ability along with isomerization and deoxygenation giving oxygen-free compounds in bio-oil. Examples are ruthenium (Ru), platinum (Pt), nickel (Ni), and cobalt (Co). For this project, Ru is used along with Pt and Co-based catalysts on titanium dioxide support. These metals help in promoting specific desired reactions to enhance bio-oil quality and stability[51].

Ruthenium (Ru) has shown great activity when supported on titanium dioxide. It has great efficiency for hydrogenation reactions meanwhile increasing the deoxygenation of compounds and stabilizing bio-oil produced. It also favors redox reactions which convert oxygenated compounds into hydrocarbons[52].

Platinum (Pt) has shown greater catalytic activity than other metals as it has a higher deoxidation range with hydrogenation. It gives high synergy to convert intermediate oxygenates to hydrocarbons. Cobalt also gives C-C coupling reactions and gives longer chain hydrocarbons thus removing oxygenated compounds. All transition metals mentioned above contribute towards C-C coupling reactions during the pyrolysis process[53].

5.5.3. Fluid catalytic cracking catalyst:

Fluid catalytic cracking (FCC) catalysts are primarily composed of zeolites and promote the cracking of higher hydrocarbons into smaller chains with more suitable compounds in the fuel range. Primarily it does cracking but other functions including isomerization and hydrogen transfer reactions are also noted with FCC. With hydropyrolysis, FCC contributes to the decomposition of biomass particles into oxygenated vapors[54].

5.6. Catalyst characterization:

Several techniques can be used to characterize catalysts prepared for parameters including surface area, pore size, particle size, and structural image for the catalysts. Brief information about the working principle is explained below:

5.6.1. Scanning electron microscope (SEM):

Scanning electron microscope (SEM) uses an electron beam having high energy to generate signals when falls on samples that are placed in the equipment. Sample parameters including chemical composition, texture, and crystalline structure can be identified. The catalyst samples in this case are analyzed using SEM to get the structure of the catalysts used[55].

The electron gun throws a beam of electron towards the sample placed and after contacting the sample, the energy difference is noted by signals generated from it. The signals can be sent to the data software to record the values and generate a structural image of the sample[55].

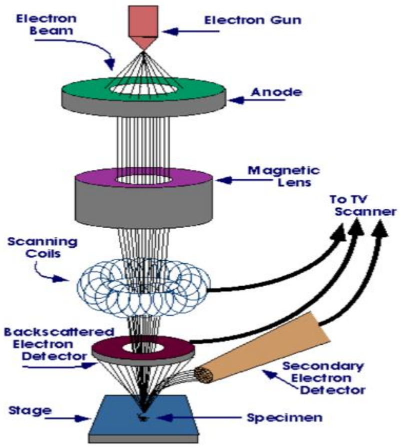


Figure 28: SEM components [55].

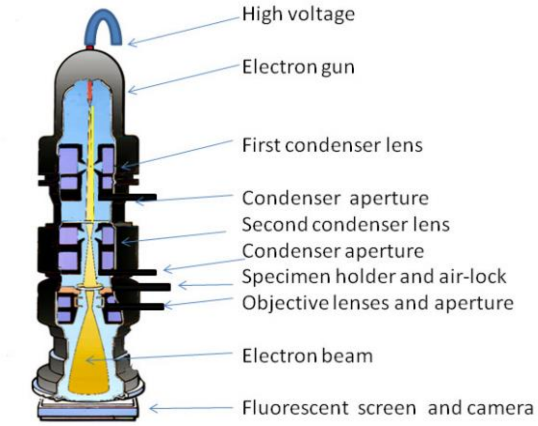


Figure 27: TEM components [56].

5.6.2. Transmission electron microscope (TEM):

Transmission electron microscope (TEM) also uses an electron beam like SEM to identify physical parameters of the sample placed like structure, chemical composition, and other properties by generating a high-intensity beam with generating image up to 2 million times magnified[56].

Electrons fall on the sample forming an image with a high voltage electron beam as it forms in SEM, the difference is energy difference forms an image in SEM but in TEM electrons after getting in contact with the sample fall on the fluorescent screen transmitted through it and form the image. Figure 27 shows TEM equipment with different parts[56].

5.6.3. Brunauer Emmet Teller (BET) method:

BET method is used to find the specific surface area of catalysts and it can be used to specify other physical parameters as well. It can also be used to find the pore size, pore volume, pore size distribution, and pore geometry for the samples as well. BET works on a method, gas molecules adsorb on the solid surface forming the basis for the method to find a specific surface area. The multilayer adsorption systems are relevant to work with BET and the gases used during the process give accurate results being inert and without reacting with the system. N_2 is commonly used for the BET process and is also done at the boiling point of N_2[57].

The BET equation given by Brunauer, Emmet, and Teller in 1938 is:

$$\frac{1}{X(\left(\frac{P_o}{P}\right) - 1)} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\left(\frac{P}{P_o}\right)$$

The equation assumes that a monolayer is formed on the solid surface by the adsorbed gas molecules. The heat of adsorption is related to C and the fraction $\frac{P}{P_o}$ is the relative pressure for the adsorbed molecules[57].

5.6.4. X-Ray Diffraction (XRD) method:

X-Ray diffraction (XRD) is used to get information about the crystalline structure, chemical composition, and physical properties of the material. The constructive interference of monochromatic X-rays forms the basis of XRD, and the sample is treated with a focused beam of X-rays. It follows Bragg's law, the diffraction of x-rays when they fall on a sample, and notes diffracted x-rays at a certain angle[58]. Bragg's law follows the equation:

$$n\lambda = 2d\sin\theta$$

where n is an integer, is the order of the reflection. λ is the wavelength of the incident x-rays, d is the distance between the planer crystal and θ is the angle of incidence.[58]

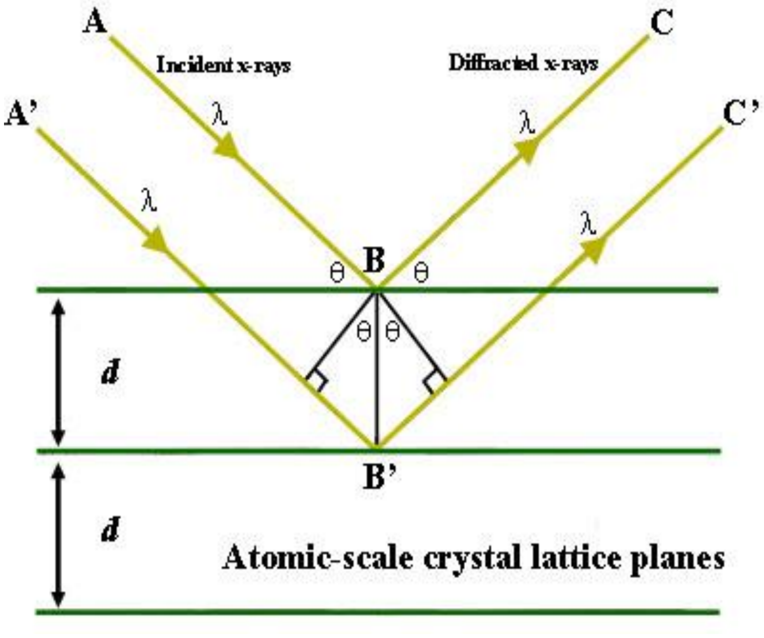


Figure 29: XRD principle for sample analysis [58].

5.6.5. Chemisorption:

Chemisorption is used to provide information about metal loading on the catalysts, metal surface area, metal dispersion, and metal crystallite size can be identified with chemisorption. A reactive gas (hydrogen or carbon monoxide) is used to reduce the sample and dosed samples with gas are then adsorbed at different partial pressures to get isotherms. Several isotherms can be noted for one sample pointing the difference in isotherms will be a point of calculation to find active metal surface area[59].

5.7. Catalyst synthesis:

Catalysts with metal loading can be prepared by following the impregnation techniques. The most common one is incipient wetness impregnation following drying, calcination, and reduction of the prepared catalysts.

5.7.1. Wet impregnation:

Incipient wet impregnation is one type of impregnation process commonly used for the preparation of the catalyst by spraying metal solution on to catalyst support. Dry impregnation is another type of the same process. Impregnation in general is depositing catalytically active metals on support materials. The solution has metal in an estimated amount to cover up the pores available on a catalyst support. An inert gas (N_2) is used as a medium to uniformly distribute the solution in droplets to cover the surface of support materials. The metal solution can be directly injected by the impregnation unit onto support eliminating the usage of big equipment. Mostly precursors having chlorides, nitrates, and sulfates are used for solutions[60].

5.7.2. Drying:

After impregnation of the metal on a catalyst support, a drying process is done to remove water from the catalyst prepared. It is normally done in an oven with a supply of air through the oven. The temperature range is between 80 - 200°C and can be placed for around 8 hours in the oven. The time and temperature of the oven influence the drying process and should be monitored, as it can redistribute the metal impregnated on a catalyst support. The heating rate is also important as too fast drying can place metals on the outer layer of the support causing precipitation so the heating rate should be adjusted at optimum level[60].

5.7.3. Calcination:

Calcination is usually done at a temperature higher than the process temperature to treat catalyst precursors in a controlled oxidizing environment. It removes binders and volatile components from precursors and also phase transformation occurs enhancing its ability for active phase and enhancing the structural integrity. The calcination process can be adjusted with a heating rate (°C/min). The temperature range is between 400 – 600°C for the calcination process and metal oxides reduce to active metals[60].

5.7.4. Reduction:

Reduction is the process used to treat impregnated catalysts and converts metal precursors into metals by removing chlorides or nitrates form the catalysts. Hydrogen is normally used for the reduction process and particular catalysts hydrazine and formaldehyde can also be used. The reduction process can be done either in the calcination oven or the reactors as well with the availability of hydrogen supply. After reduction, the catalysts are left with active metals so hydrogen concentration should be monitored and can be passivated by having a small oxidation layer over the catalysts[60].

6. Experimental Section:

The pilot plant consists of reactors, gas filters, and condensers along with a screw feeder. Two reactors include a pyrolysis reactor and secondary upgrading reactor. Modification to existing sections along with changing completely was done.

6.1. Biomass feeder:

The biomass feeder consists of two hoppers including a stirrer attached to the first hopper to get the biomass agitated continuously and does not let biomass stick to the hopper walls. The second hopper is smaller as compared to the first one and it leads the biomass towards the pyrolysis reactor. The agitator is a flap type and is attached to mechanical gear. The screws for both the hoppers are attached to mechanical gears as well and the speed can be adjusted by the PID controller according to the feeding rate required for experiments. The screws are also calibrated for the biomass particle size (250-500μm) so that biomass in the pyrolysis gets equal heat transfer and the uniform process occurs and no biomass is left unreacted or takes much time to get pyrolyzed. Also, nitrogen flow is given at the rate of 10 nL/hr to have constant pressure in the feeder to have a constant feeding rate and to avoid back flow from the pyrolysis reactor towards the feeder.

The biomass feed rate was also calibrated manually to ensure the mass flow rate as it can be different from the set point. It has been noted that for a set point of 20 gm/hr feed rate, the actual feed coming out of the feeder was around 18 gm/hr. So, the flow rate was double-checked before every experiment. Also, for 40 gm/hr the actual was around 36 gm/hr.

Figure 30: Biomass to aviation fuel pilot plant used for experiments.

6.2. Fluidized bed reactor:

The fluidized bed reactor is where the pyrolysis reaction takes place for the biomass coming from the feeder. Both conventional pyrolysis and hydropyrolysis processes can be done in the reactor as the analogy is the same for both processes, depending on the flow of hydrogen being given for hydropyrolysis. Hydrogen flow is controlled by the PID controller. The material for the reactor is stainless steel (SS310) with a maximum temperature range of 650^{o}C. Also, there are heaters installed around the fluidized bed reactor to heat the reactor, and the position of heaters such that there should be no temperature difference along the reactor. Thermocouples have been installed inside the reactor to have continuous temperature surveillance and it should keep the temperature at a given set point. There is a joint at the top of the reactor that can be opened to add sand or FCC inside the reactor. There is also a bed holder placed inside to hold up the fluidized bed and the height of the bed holder is adjusted such that the fluidizing medium covers the opening of the line coming through the feeder and the gas flow is adjusted to have a fluidized bed. Nitrogen and hydrogen flow from the bottom part of the reactor toward the top of the reactor. The sand is also screened with particle sizes in a range of 250-500µm. As for this project, spent FCC catalyst was also used in the pyrolysis reactor so the bed holder mesh size was adjusted to hold the FCC catalyst also because of its fine particle size than sand.

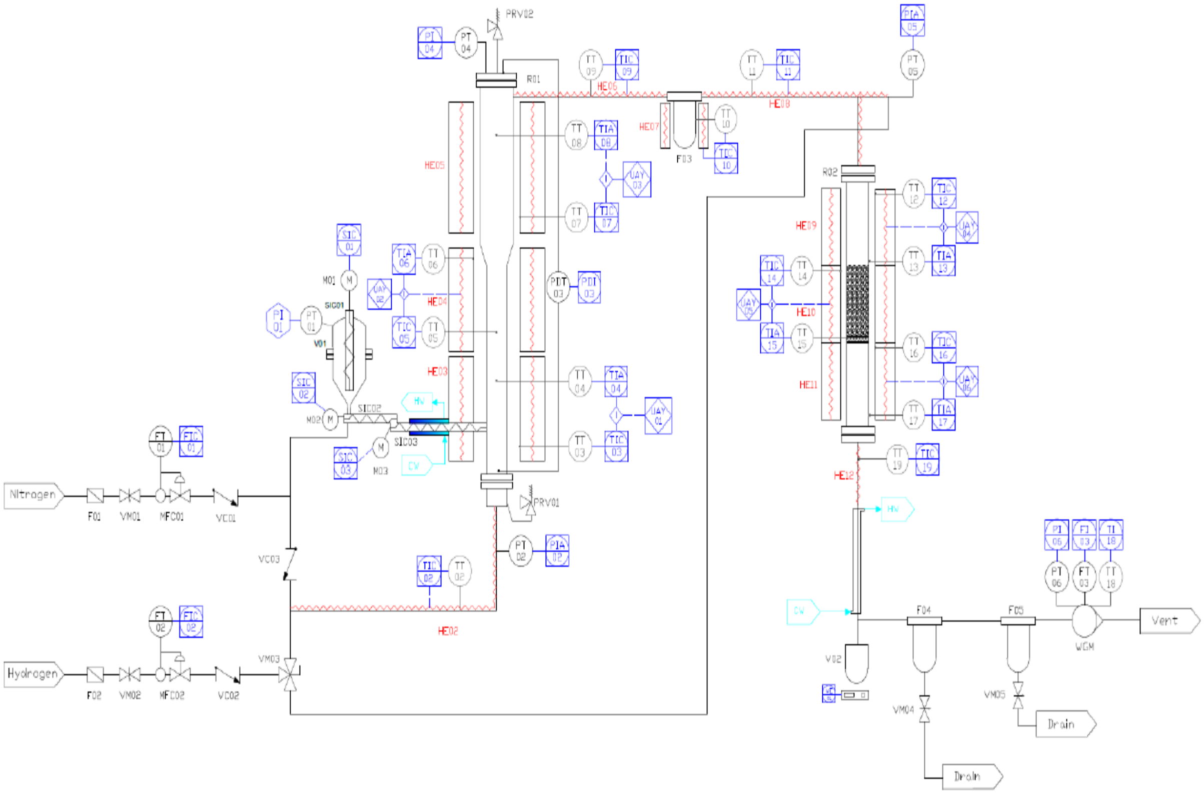


Figure 31: Biomass to aviation fuel pilot plant P&ID.

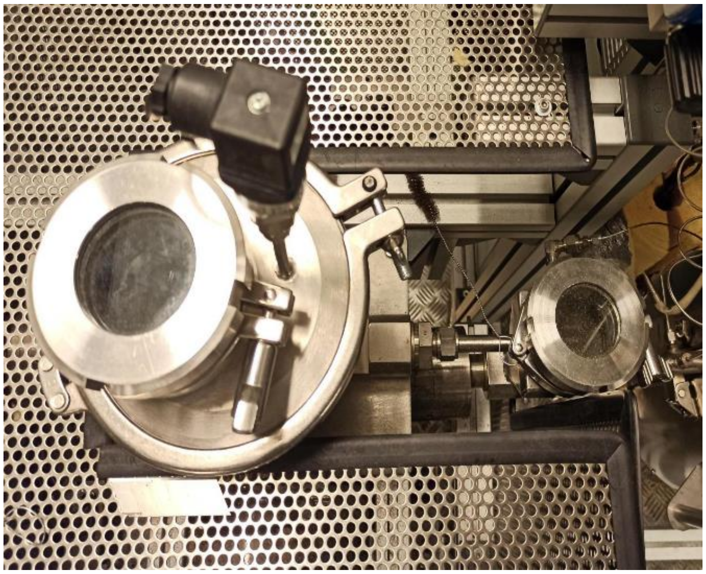


Figure 33: Biomass screw feeder.

Figure 32: Chilling unit for condenser.

Figure 35: Hot gas filter with insulation.

Figure 34: Pyrolysis reactor connected.

Figure 37: Upgrading reactor.

Figure 36: Primary condenser.

Figure 39: Glass condensers.

Figure 38: Solvent bottle with sinterer.

6.3. Gas filter:

The filter for the gases to clean up after the pyrolysis process takes place in the pyrolysis reactor comes downstream of the reactor where the particulates coming with pyrolysis vapors and or char is filtered out before the vapors go to the fixed bed reactor for the upgradation process. The filter installed can hold up particles with ≥100μm and passes through clean vapors so that no contamination goes towards the upgrading catalyst and the performance of the catalyst for upgrading does not affect it. It gives the advantage of removing particulates before reaching catalysts so to avoid losing catalytic activity with coke deposition. The gas filter operated around 350^{o}C.

6.4. Fixed bed reactor:

The second reactor with an upgrading catalyst in it is a fixed bed with a catalyst placed in the reactor equal to the height of the reactor to have more contact time for the pyrolysis vapors with the catalyst. The reactor is made with stainless steel (SS316) and the diameter of the reactor is 1.66 cm. The catalysts used for the upgradation are mostly in pellet form and have interstices in between pellets which gives good contact with pyrolysis vapors.

The maximum temperature range for the reactor is 450^{o}C and there are thermocouples (K type) installed in the reactor to have continuous monitoring of temperature in the reactor and the set point adjusted by PID controller just like in a pyrolysis reactor. The heaters were also installed to heat the reactor and to have uniform heating throughout the reactor. There is no external gas flow through the reactor and the downstream of the reactor is attached to the condensing unit.

6.5. Condensers:

The condenser is attached downstream of the fixed bed reactor and is used to condense vapors coming from the fixed bed reactor. The condenser is shell and tube type with water being used as coolant. There is also a chilling unit separately with a coolant (ethylene glycol) mixed with water which is used as the primary coolant in the condenser to liquify the vapors coming from the reactor. The vapors enter from the top of the condenser and a collection unit is attached at the bottom of the condenser for liquid holdup. Two additional glass condensers with coolant inside of the glass spirals are also used for enhanced condensation of vapors and a solvent bottle is also attached after glass condensers to dissolve hydrocarbons in it. There is also a gas line going out to the vent and is connected to GC TCD for light hydrocarbons which are not condensable and pass through the condenser out to the vent.

6.6. Chilling unit and PD pump:

There is a chilling unit with ethylene glycol (50%) as a coolant used for the condensing purpose and water cannot be used below 4^{o}C. With ethylene glycol, the condensing can be done at -20^{o}C but for actual operational conditions, it can be used at -7^{o}C to avoid freezing of water in condensers. Also, the PD pump is used to circulate acetone throughout the condenser to clean up residual liquid left before running new experiments to avoid contamination.

6.7. Solvent bottle:

A solvent bottle is also attached after glass condensers to capture and dissolve compounds that are not condensed in condensers and can be captured in a liquid solvent. The solvent choice is made with its affinity to capture oxygenates and hydrocarbons. For the experimental purpose, GVL is being used as a solvent with its ability to dissolve both hydrocarbons and oxygenates as well.

7. Pilot plant working:

The plant has been used to run experiments to get results about catalyst efficiency to upgrade vapors and get desirable product distribution. Some steps should be followed to perform experiments without having any problems and to avoid uncertainty before or after the experiment. The experiment parameters just discussed in the section above can be controlled with the help of a PID controller and the monitoring for pressure and temperature was done by the data acquisition in the software to continuously monitor the pressure and temperature. Also, the temperature doesn't change much from the set point, the pressure however needed to be looked at very carefully while running the experiments as it can increase very quickly and can be dangerous if it reaches above the safety limit causing leaks of flammable and toxic gases. The temperatures for different sections of the plant are given below in Table 6 as thermocouples are installed to provide information about it. There is also a safety check that comes into effect, if the pressure inside the reactors goes above 1 bar the rig turns off automatically and all gas supplies go off as well.

Table 6: Thermocouples position on pilot plant.

	Thermocouple	**Thermocouple position**	**Temperature (ºC)**
1	TIC02	before fluidizing bed (gas preheat)	500
2	TIC03	bottom section of fluidizing bed	500
3	TIC05	middle section of fluidizing bed	500
4	TIC07	upper section of fluidizing bed	500
5	TIC09	between fluidizing bed and filter	350
6	TIC10	gas filter	350
7	TIC11	between filter and fixed bed	350
8	TIC12	top section of fixed bed	400
9	TIC14	middle section of fixed bed	400
10	TIC16	bottom section of fixed bed	400
11	TIC19	before condenser	400

The temperature range was maintained at given temperatures for experiments and the pressure limit is 0.7 bar for experiments. Details about the experimental procedure are explained.

7.1. Experiment procedure:

As the rig was already in use with experiments performed before, it is important to make sure that the rig is clean before staring an experiment to be sure that no traces from previous experiments would come in with the new experiment and can alter the results. A detailed experimental procedure is given below which has been followed step-wise to perform the experiments.

7.1.1. Rig cleaning:

Cleaning of the rig includes cleaning of pyrolysis reactor, cleaning of upgrading the reactor, cleaning of condenser, and burning the carbon trapped in rig pipes by passing oxygen at elevated temperatures. For the condenser, acetone is used to clean it for any sticky compounds left in there. The experiment will start with the cleaning of a fluidized bed reactor. The coupling between the gas line and fluidized bed reactor, with the help of a spanner, will be opened and collect all fluidizing material in a bucket that was used in earlier experiments. Further, reinstall all the couplings with a gasket in the system as it was before and make it airtight properly. The seals should be placed to have proper fitting for the joint and to have leak proof assembly.

Opening the coupling between the fluidized bed reactor and the safety release valve line, which is above the reactor, fluidizing materials will be added with the help of a funnel. Further, it is again connected tightly as it was before. Note that the fluidizing material should be 3 times the size of the diameter of the pyrolysis reactor and there is a bed holder at the bottom of the reactor which holds the fluidizing medium.

There is also a need for a catalyst to upgrade the bio vapors which is generated from pyrolysis reactions. The upgrading reactor will be opened from the coupling which is connected to the pipe from the filter and loosened the fitting from the bottom so it can be turned down and can empty the reactor. Further, a catalyst will be added to the reactor till the full volume of the reactor with the help of a funnel. All fittings are connected as they were before and tightened up to avoid leakage.

Cleaning of the bottom part of the condensing unit where bio-oil is collected. With the help of acetone, it should be cleaned and reinstalled in the same place as it was before. Cleaning of the condenser pipe after upgrading the unit will be done by circulating acetone solution through a peristaltic pump and collecting it in a separate bottle. Before circulating acetone solution in the pipes, close the valve which is connected to GC lines for gas samples. It should evaporate which is left in the pipe after cleaning through the nitrogen supply for a few minutes.

7.1.2. Procedure for starting experiment:

To perform experiments on the rig, an SOP should be followed to complete the experiment and to avoid any mistakes while running the experiment. The following steps should be followed:

1. Check for the biomass in the feeder. It should be more than 150 grams. If it is there perform PHT (pressure hold up test).
2. A pressure holdup test has been performed with nitrogen gas for fixed pressure at (0.7 bar) and checked for a few minutes which ensures that the system is airtight. If it is fluctuating, check for the leakage through flame detector.
3. Heating of the reactor has been done in the presence of nitrogen. For this, first, open the nitrogen valve and close the air valve so nitrogen flows into the system. Click on the (set config) on the screen and load ‘heat’ by switching on the manual switch for heating.
4. Heating of the reactors has been performed with air. It also cleans the reactor through the combustion of the remaining residue in the reactor and pipeline from the earlier experiment. It will take almost 2 hrs.
5. After 2 hours, close the air valve and open the nitrogen gas valve at 1 liter per hour for 5 minutes and then slowly open the hydrogen gas valve at 1.5 liter per hour.

6. Switch on the chiller in which ethylene glycol solution is used. The set temperature for the chiller is 0.5°C.
7. Before using in a feeder, biomass should be placed on the aluminum foil and heated at 150°C for 3 to 4 hours minimum. This will remove most of the excess moisture.
8. Switch on the feeder at the desired feed rate of beach wood of particle size 250 to 500µm.
9. The experiment can be run for 4 hours or more in which after every 20 minutes gas will be analyzed through GC and bio-oil will be analyzed using GC-MS.

7.2. Bio-oil analysis:

After the experiment bio-oil was collected from the collection pipe and condensers, and it separated into aqueous and organic phases. The separation is based on the difference in density and separation in sample vials. Note down the weight of empty vials and then weigh the vials with bio-oil. The yield of bio-oil can be calculated by dividing the weight of bio-oil by the weight of biomass fed during the experiment.

7.2.1. Karl Fischer titration:

Karl Fischer titration is used to find the amount of water content in aqueous phase. The steps mentioned are required to perform KF titration.

1. Do the standardization of the Karl Fisher setup before starting.
2. Filter the sample using a 20µm filter.
3. Dilute the aqueous phase of bio-oil 10 to 15 times with pure ethanol.
4. Take a few ml of filtered sample in a syringe and put it into the titrator of Karl Fisher setup and enter the weighed value sample which is put on the titrator.
5. Press the start button after entering the value of the amount which is entered.
6. It will tell the percentage of water in the sample you injected.

7. Calculate the mass fraction of water in the initial one.

7.2.2. GC analysis:

GC FID analysis for liquid samples:

1. Collect a clean vial of GC-MS to fill the sample.
2. Fill the aqueous phase of bio-oil into the GC vial under the fume hood.
3. Put your sample in the designated position for the GC FID system and start the process by selecting the methods for different samples.
4. Reverify whether the FID temperature reached 250°C.
5. After 225 minutes, the analyzed sample can be checked for results.

GC TCD/FID online analysis for gases:

1. Press the start button while entering the sample details such as name, date, etc., and set the frequencies at which time you want to take a sample.

2. Tick mark the continuous analysis option so that the equipment continuously analyzes the sample after regular intervals.

3. It is the online detection of gas so it will analyze the pyrolysis vapor every 20 minutes and store it. It can detect carbon monoxide, carbon dioxide, hydrogen, methane and nitrogen, and other light hydrocarbons**.**

7.3. Experiments detail:

The experiments were performed in a sequence with an analogy to understand the working of the pilot plant and the ability of catalysts to upgrade vapors. Several experiments were also completed to see the lifetime of catalytic activity of the catalyst. There were also changes made to the rig accordingly to get optimum results.

Table 7: Experiments details with process conditions.

Experiment	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Fluidized bed reactor (ºC)	500	500	500	500	500	500	500	500
Fixed bed reactor (ºC)	400	400	400	400	400	400	400	400
Fluidizing medium	Sand	FCC	FCC	FCC	Sand	FCC	FCC	FCC
Catalyst	-	-	TiO_2	Ru/TiO_2	Ru/TiO_2	Ru/TiO_2	Ru/TiO_2	Co/TiO_2 + Pt/TiO_2
Hydrogen (l/min)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Nitrogen (l/min)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Feed rate (gm/hr)	20	20	20	20	20	20	40	40

The process conditions are maintained for all experiments and the catalysts were changed to have a comparison for the catalytic activity. Hydrogen and nitrogen were also given in specified flow for fluidization and the feed rate was also maintained two experiments were performed with an increased fee rate to see the effect of less residence time.

Figure 40: Biomass to aviation fuel pilot plant without gas filter.

7.4. Technical issues faced:

While running experiments there were technical challenges that have been faced and identified in between experiments. The challenges faced during experiments are mentioned:

1. The most common issue that arose during experiments was pressure build-up between fluidizing bed and gas filter. There was crystalline waxy material around the walls of the pipe and at the top part of the gas filter causing pressure buildup. A mesh rolled up and placed in a pipe adjusted for this issue, although it was not a permanent solution, the pressure build-up was reduced and experiments were performed for a longer time than before.

2. There was fluctuation observed in the screw feeder while running experiments. The feed rate was then double-checked by running feed for one hour and weighted the biomass collected in a bucket. There was a difference in actual feed coming out at an actual set point, so the set point of 20 gm/hr feed rate was 18 gm/hr in actual.

3. Gas leaks were detected from joints between the fluidizing reactor and gas filter and the top of the upgrading reactor with alignment. Mainly the seals were damaged by continuously opening of filter for cleaning. The seal was replaced almost every time after cleaning the filter and the alignment was adjusted for upgrading the reactor as the thread was also damaged.

4. The gas filter was not covered properly and that caused the temperature difference. The top section was covered with a waxy crystalline layer during experiments and this issue was reduced by covering the top section of the gas filter which was uncovered before.

5. Nitrogen is supplied to the rig by a central gas supply, and it was noted that during experiments there was a fluctuation in gas amount. It was due to a change in pressure from the main supply, but it was not a recurring issue.

6. The porous sinterer in the solvent bottle got blocked with vapors passing through it and it caused pressure to build up in the complete rig causing experiments to stop. This sinterer design was changed and a porous blockage was removed from the glass rod to avoid pressure buildup.

7. The cleaning of glass condensers was a big problem, and this was sorted out by modifying the bottom of glass condensers having a threaded cap to clean up and remove bio-oil after experiments.

8. The bottom of the pyrolysis reactor got a leak after the screw was damaged and it was replaced with a new screw, having a packing seal in between screws gave extra support to avoid leaks.

9. A rotary evaporator was used to separate bio-oil from the solvent used to clean condensers. The cooling water pipe was broken, and the pipe connected to the suction pump was also broken and was changed before using it.

8. Results and discussion:

The samples analyzed for gases, bio-oil, and modifications made to get more mass yield all are discussed in this section. The catalysts used in the upgrading process are also prepared onsite and has explained as well.

8.1. Catalysts:

The catalysts used in experimentation were prepared using metal precursors and titanium dioxide (TiO_2). Three bimetallic catalysts were prepared to have 0.5 wt.% of metal loading. All metals were impregnated on titanium dioxide support using the wet impregnation technique.

Titanium dioxide (TiO_2) was calcined before impregnation to remove any volatiles and binders present in it at 450°C, more than the process temperature. It also helps in ordering the surface for catalytic activity.

Table 8: Titanium dioxide (TiO_2) calcination conditions.

	Temperature (°C)	Ramp rate (°C/min)	Hold-up time (hr)
Titanium dioxide (TiO_2)	25-450	1.5	4

High-temperature furnace having a max range of 1100°C was for calcination both for pure titanium dioxide samples and for catalysts prepared after impregnation. The ramp rate was set to reach the desired temperature and held up to maintain the temperature at the set point.

The precursors used for impregnation are:

Table 9: Metal precursors used for catalysts impregnation.

Metal	Precursor
Ru	$RuCl_3.H_2O$
Pt	$PtCl_4$
Co	$Co(NO_3)_2.6H_2O$

The solution of the precursor was prepared with the required amount of metal present and calculations were made based on the requirement. The calculation is explained in the appendix. For the precursor solution, a beaker with a magnetic stirrer was used along with distilled water and placed on the magnetic plate for it to dissolve all of the precursors. For impregnation, a syringe pump was used in the presence of N_2 to uniformly spread the liquid onto titanium dioxide pellets which are 3mm in size.

The drying of impregnated pellets was done in a drying oven with a temperature set at 80^oC and placed for 8 hrs. It helped in removing any excess moisture coming from impregnation and drying up the catalyst. The same conditions were used for all catalysts prepared and then they were calcined in HTF.

Table 10: Catalysts calcination conditions.

Catalyst	Temperature (^oC)	Ramp rate (^oC/min)	Hold up time (hr)
0.5wt% Ru/TiO_2	25-450	2	4
0.5wt% Pt/TiO_2	25-450	2	4
0.5wt% Co/TiO_2	25-450	2	4

Calcining after impregnation removes all the additional compounds apart from the active metal like chlorides and nitrates in this case. The reduction was done by upgrading the reactor of the rig with hydrogen flowing at 1l/min and the catalysts were reduced for 5hrs before using them for experiments.

Ru/TiO_2 was used several times to check the catalytic activity for several experiments and Pt/TiO_2 along with Co/TiO_2 were used to have a comparative study of the catalytic activity of the catalysts. The experiments details above also show that four experiments were performed without regenerating the same catalyst. The details will be discussed in the liquid analysis section. The run time for Ru/TiO_2 counts for all experiments which are successful and analyzed completely and those which are failed as well.

The experiments with Ru/TiO_2 were performed with sand and FCC as fluidizing medium and the runtime for all experiments is given in Table 11:

Table 11: Experiments performed with Ru/TiO_2.

	Catalysts	Runtime (hr.)
Exp 4	FCC + Ru/TiO_2	14
Exp 5	Sand + Ru/TiO_2	12
Exp 6	FCC + Ru/TiO_2	6.5
Exp 7	FCC + Ru/TiO_2	5

A few experiments which were started using the same catalysts failed because of pressure build-up and freezing in the first condenser pipe, which also accounts for the runtime as exp 6 and exp 7 were performed after those failed experiments, and the results were generated. All other experiments were performed with a single run for other catalysts.

8.2. Mass balance:

The experiments performed were analyzed for different products obtained including solid, liquid, and gas phase products. With the focus on increasing mass yield for the pilot plant, several changes were made for different experiments. The changes made also focused on increasing liquid product yield and capturing as maximum as possible. Solid products have char and coke, and liquid product includes aqueous and organic phases. There is also unknown mass which was not quantified and thus the overall mass yield includes all products.

Table 12 explains the working conditions for experiments and changes made for the experiments. Changes made to condensing section, gas filter, and chilling unit are all accounted for in the experiments.

Table 12: Rig arrangement for experiments.

	Rig arrangement	**Purpose**
Experiment 1	performed with sand without upgrading catalyst.	to generate results for comparison
Experiment 2	performed with FCC without upgrading catalyst.	to get results for comparison with sand
Experiment 3	with FCC and TiO_2 and two glass condensers	to see the effect of TiO_2 on bio-oil
Experiment 4	with FCC and Ru/TiO_2	to see the effect of Ru/TiO_2 on bio-oil
Experiment 5	with sand and Ru/TiO_2	to examine the difference between sand and FCC with Ru/TiO_2
Experiment 6	with FCC and Ru/TiO_2	to examine the catalytic activity of Ru/TiO_2
Experiment 7	with FCC and Ru/TiO_2	to examine the catalytic activity of Ru/TiO_2
Experiment 8	with FCC and Co/TiO_2 + Pt/TiO_2	to examine the comparison with Ru/TiO_2

Sand and FCC were used as a fluidizing medium in pyrolysis reactors and all other catalysts mentioned were used ex-situ in upgrading the reactor. There was a significant addition of mass yield after adding a glass condenser. The chilling unit was also used at a lower temperature around -7°C for condensation.

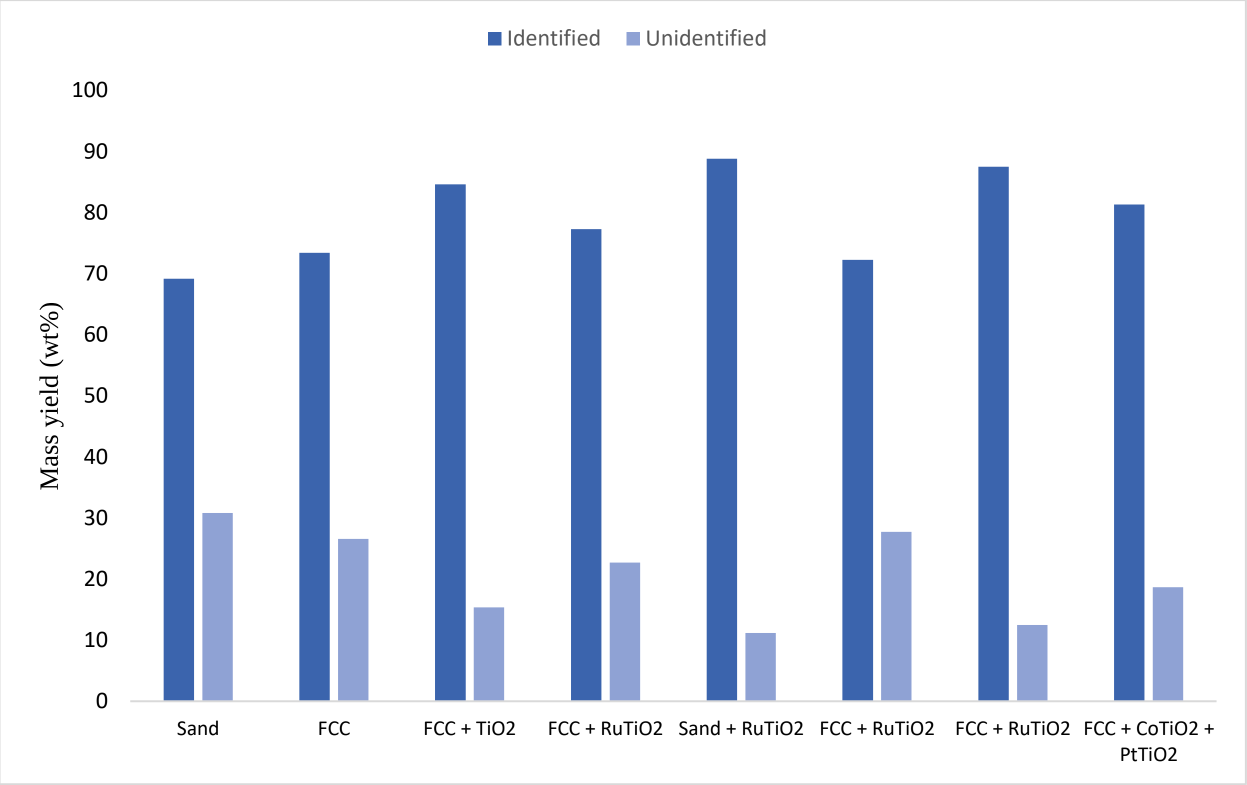


Figure 41: Overall mass yield comparison for identified and unidentified mass.

It can be seen that there has been an increase in identified mass, that is because of the addition of additional condensers. The uncaptured mass went down from 31% to 11% from experiment 1 to experiment 5. The highest mass yield was obtained with Ru/TiO_2 + sand and then Ru/TiO_2 + FCC has almost the same mass yield obtained. The lowest was for experiment 1 (sand only). All other experiments have mass yields between 75% to 85% which are reasonable amounts identified. The tubing for the coolant was also covered up with insulation pipe to avoid heat transfer before the coolant enters the condensers.

The identified mass was further analyzed in different phases primarily gas, solid, and liquid samples. Although all phases can be further analyzed for desired parameters depending upon the requirement. Liquid samples were analyzed and will be discussed in the liquid analysis section. Figure 42 gives us detailed information about the different phases obtained in products.

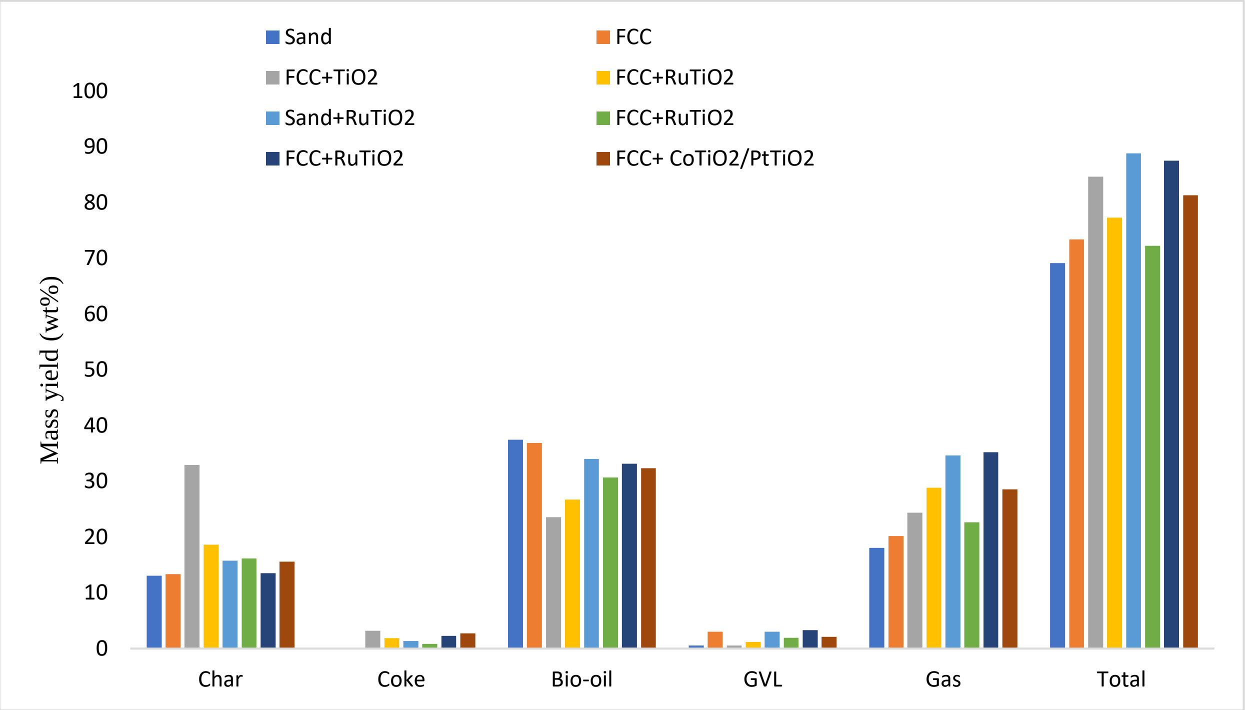


Figure 42: Mass yield comparison for different products analyzed.

All experiments were performed in a systematic sequence to have a comparative study, sand and FCC were used without any upgrading catalysts therefore there is no coke for those experiments. Char is collected from a pyrolysis reactor, and it is in the range of 13-20%. Char from exp 3 with pure TiO_2 is very high at 33%, it can be noted that the heating rate would be a cause for high char value. All other experiments have char in the normal range for fast pyrolysis as discussed in section 3.1.4. It is also understandable as the process conditions were the same for all experiments and the difference in char would be by heat transfer, also temperature variation and pressure buildup in the pyrolysis reactor would increase the char production. Coke is also different for pure titanium dioxide and metal-impregnated catalysts. Pure titanium dioxide has a high tendency to have more coke and the addition of metals to titanium dioxide can reduce coking on the catalyst due to changes in surface properties and chemical reactions[49]. Pure titanium dioxide has coke around

3.2% which is highest than others. Ru/TiO_2 has coke from 0.5-2.3%, also 2.3% occurred as the gas filter was removed before the experiment and there was no blockage to remove particulates going to the catalyst. Similarly, 2.7% coke for Co/TiO_2 + Pt/TiO_2 is also high as the gas filter was removed. Normally with metal supported titanium dioxide catalysts have around 1-2% coke. Char was weighed by the difference in mass of fluidizing medium before and after the experiment and coke is also weighed by weighing the catalysts before and after the experiment. Solid products, both char, and coke can be analyzed using techniques like elemental analysis, and thermogravimetric analysis (TGA) to identify the nature of the product. There is also secondary char formed during the process with secondary reactions occurring and that can also be analyzed. So, TiO_2 has a greater tendency than metal-supported catalysts to produce solids.

The gases produced are also noted for different catalysts used. It can be noted that Ru/TiO_2 has the highest gas yield around 35% with FCC and with sand it is around 34.6%, both are relatively close and higher than the rest. Co/TiO_2 + Pt/TiO_2 has a 28.5% gas yield following pure TiO_2 having 24%. It can be stated that ruthenium has more capability to produce gases than other catalysts used. Ru/TiO_2 was used for several experiments so it can be disregarded the difference in gas yield in experiment 6.

Bio-oil samples collected from all condensers and mass collected from GVL also accounted for mass yield. Typically, bio-oil has two distinct phases, aqueous and organic phase. The organic phase is also called heavy oil as it has higher carbon compounds (C_6-C_{15}). The aqueous phase is typically 90% water and all samples collected were clear white KF titration was also done for the samples giving information about the water content present in the samples which will be discussed in the liquid analysis section. The aqueous phase has chemical species like acids, and alcohols, along with phenols and a small amount of ketones. All these compounds are in the range of C_1-C_6.

The organic phase includes heavy oil collected after the separation of phases in catalytic upgraded samples. For experiments 1 and 2, there was no phase separation and single-phase oil was collected. It can be noted that for experiments 1 and 2, bio-oil yield was more than in other experiments and gas yield was less than in other experiments. The reason is as oxygen is still present in bio-oil and it was not separated from bio-oil, so the amount of bio-oil was more. The selectivity based on bio-oil yield is Sand > FCC > (Sand +Ru/TiO_2) > (FCC + Ru/TiO_2) > (FCC +

Co/TiO_2 + Pt/TiO_2). It can be noted that experiment 8 was performed with a dual bed having 50% Co/TiO_2 and 50 % Pt/TiO_2. The addition of condensers and solvent increased the overall mass yield from 65% to 89% which is a considerable increase, although pressure buildup was also considered for experiments runtime. It is observed that the more runtime for the experiment the more amount of heavy oil obtained after experiments and removing the gas filter stabilized the pressure buildup, the catalysts were prone to coking quickly. GVL was attached after condensers and before the gases go to the gas sample, the color change was significant for all experiments which can be due to uncondensed vapors passing through GVL and the mass obtained also is evident. The mass yield obtained from GVL is from 0.5-3.3%.

The uncaptured mass can be due to loss in between the reactors and pipes, condensation in pipes, and vapors passing through condensers without condensed can all be accounted for bio-oil, as the bio-oil yield is in a range around 34% and uncaptured mass added to this amount will make up bio-oil around 50% which would be equal to amount from literature.

8.3. Gas Analysis:

Gas samples were analyzed for experiments using on-site GC FID/TCD. The samples were injected after every 20 minutes, and the equipment was preset accordingly. Vapors pass through condensers and solvent enters the gas line which connects to GC for gas analysis and then it goes out. Primarily the gases include CO, CO_2, CH_4, and C_2-C_6. Ethane and ethene are both accounted for in C_2, propane, and propene in C_3.

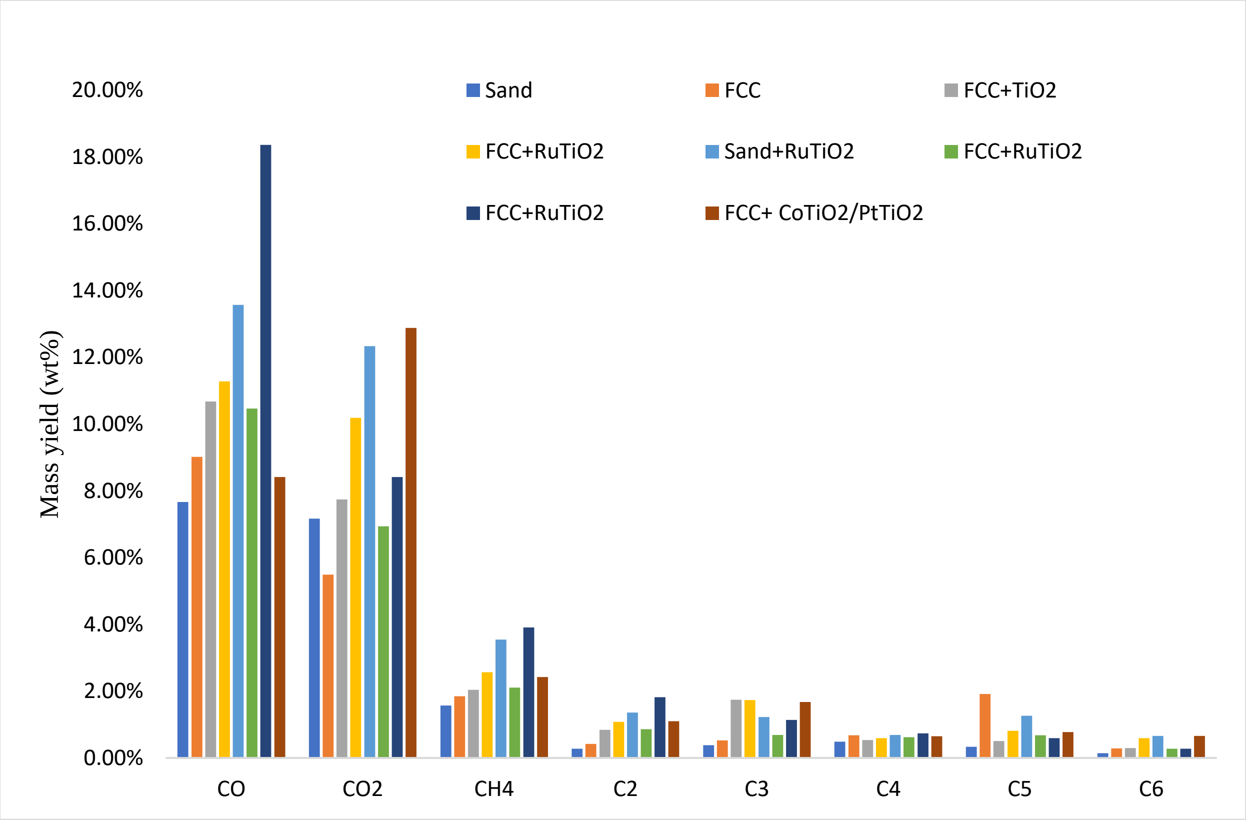


Figure 43: Gases comparison for different catalysts on weight basis.

CO and CO_2 are the main constituents of gases along with methane. Also, changing catalysts mainly affect these two gases and a slight difference has been observed for light hydrocarbon gases. It can be seen for experiments 1 and 2, CO, CO_2, CH_4, C_2, and C_3 gases are considerably lower than other experiments. It is as if there is oxygen remaining in bio-oil and no catalyzed reactions promoted the formation of CO and CO_2. There is a sharp increase in catalyzed experiments with additional reactions that takes place as discussed in section 4.1. Those reactions include decarboxylation, and decarbonylation, along with water gas shift (WGS) reactions which promote CO, CO_2, and CH_4. This is evident from Figure 43 that using upgrading catalysts promotes methane formation along with CO and CO_2. C_5 is high for experiment 2 with FCC, it can be said that FCC promotes cracking reactions of higher carbon chains and releases lower hydrocarbon gases which are noted[54].

For catalyzed experiments, the highest gas yields were obtained for (FCC + Ru/TiO_2) > (Sand + Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2) > (FCC + TiO_2). As hydrogen is supplied for experiments, hydrogenation along with cracking reactions and FCC as itself a zeolite has a high tendency to promote CO and CO_2. Methane formation by methylated compounds having oxygen gives water as a byproduct[19]. It is also considerable to note that the line connecting GC for samples was shortened and it also increased the gas amounts by reducing residence time in line.

Acids and alcohols and aldehydes upon breaking give away CO and CO_2 also increases C_2-C_3. As these species are not detected in heavy oil, it is noted that all these species are converted to gases and higher chain compounds. Acetic acid is detected in a considerable amount, and it goes in different paths generating different species which are converted into species that also help in continuing reactions. Hossein et. al and Haijun et. al. studied pathways for acetic acid as given in Figure 44[61].

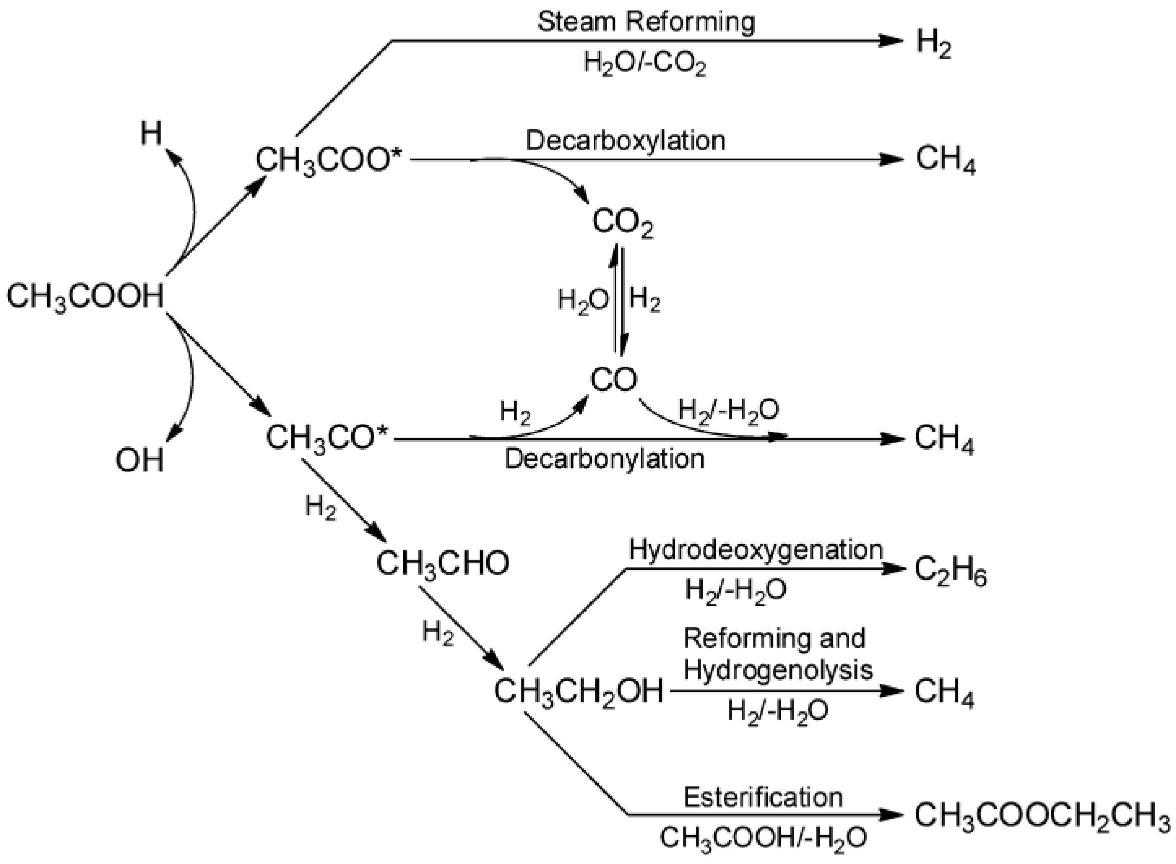


Figure 44: Acetic acid decomposition to form different products [61].

Acetic acid upon hydrogenation and deoxygenation makes intermediates which are also found in liquid analysis. Intermediates like ethanol give away methane and ethane. It also undergoes decarboxylation and decarbonylation to form CO and CO_2[61] [62]. It is the common reaction mechanism followed in all experiments to have CO and CO_2 as the most prevalent gases and lighter hydrocarbons are produced by intermediate reactions that occur during the breaking of biomass. Ethane is highest for (FCC + Ru/TiO_2) > (Sand + Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2) > (FCC + TiO_2). TiO_2 also has high hydrogenation ability and thus has a considerable amount of ethane and propane. It can be noted that water is released in each intermediate reaction to produce gases and thus it is also prevalent to have high methane as well.

Ketonization and aldol reactions are also significant in catalyzed reactions and oxygenate and acetone are the main products formed with these reactions. Acetone comes from acetic acid which is formed by the decomposition of hemicellulose. From Figure 43, it can be noted that CO_2 is highest for (FCC + Co/TiO_2 + Pt/TiO_2) and (Sand + Ru/TiO_2) denoting that the ketonization ability of these catalysts is prominent. CO is highest for (FCC + Ru/TiO_2) which indicates that CO_2 is reduced to CO over metal catalysts. The reduction can be by oxygen transfer reactions on the metal oxide's surface when CO_2 contacts the catalyst's surface.

Propane is highest for (FCC + TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2) > (Sand + Ru/TiO_2) > (FCC + Ru/TiO_2). Propanoic acid is also detected in all samples along with its derivatives and it goes to propane in gases along with the release of water that would make up the aqueous phase in bio-oil collected from experiments. Titanium dioxide has high hydrogenation ability and with FCC it can have a strong influence on producing large amounts of water along with gases[63].

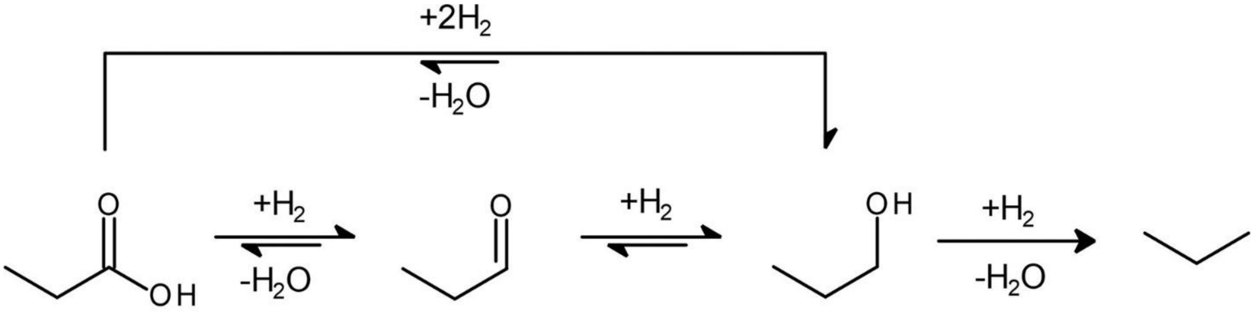


Figure 45: Formation of propane by propanoic acid [63].

Hydrogenation and deoxygenation are prominent in the conversion of propanoic acid. Intermediate compounds including acetone are also formed and are detected in all heavy oil samples. Acetone formation also follows the same pathway and water also removed in all intermediate steps increases its amount also in liquid samples.

Decarboxylation is the preferred reaction scheme as it is desired to have more CO_2 than CO in the gas phase, removing more oxygen at the expense of carbon, so (FCC + Co/TiO_2 + Pt/TiO_2) has a high tendency to have more decarboxylation reactions than decarbonylation. All other catalysts contain CO more than CO_2. FCC also influences methane formation and Ru/TiO_2 has more methane and shows its ability to continue reactions and give off water.

8.4. Liquid Analysis:

Bio-oil samples were collected after experiments from the main collection pipe and glass condensers attached to the rig. The samples were primarily two distinct phases as mentioned before, an aqueous phase which is clear like water, and an organic phase which is oil having all the chemical species. Liquid samples were analyzed using GC-MS for the retention time of chemical compounds, and then GC FID was used to match and identify the peak areas using data from GC-MS. Almost 110 compounds have been detected in the heavy phase including different classes. The aqueous phase was also analyzed for water content with KF titration and is discussed below, around 90% is water and it was difficult to analyze the samples with less chemical species. The matching was done by matching peaks retention time and physical shapes also to avoid errors. The figure shows different functional groups identified in heavy oil samples. The distribution was based on weight fraction for all functional groups and all species combined in the same functional groups.

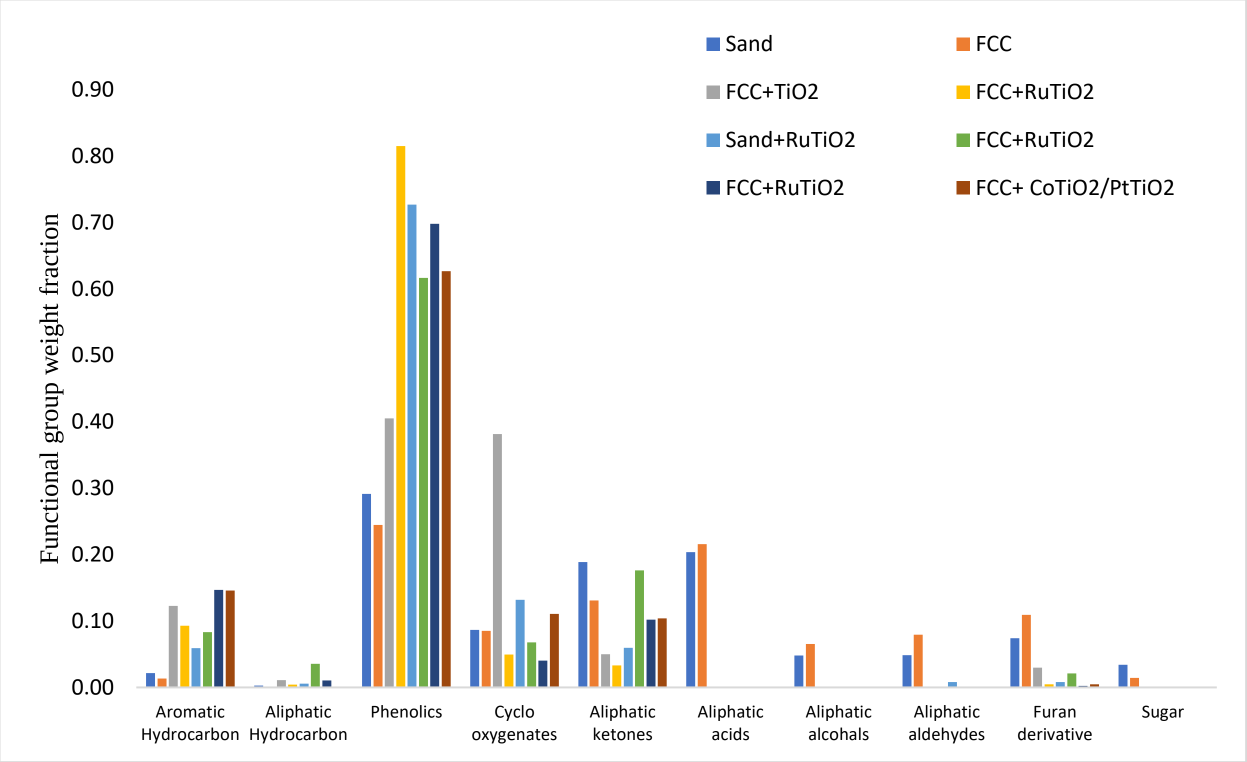


Figure 46: Functional group analysis for bio-oil samples.

For all experiments, phenolic compounds were the main constituent of the oil phase, along with ketones and cyclo-oxygenates. Aromatic hydrocarbons were also detected in a considerable range for all catalyzed experiments and small amounts of furans were also detected for all experiments with more amounts for un-catalyzed experiments[64]. Other functional groups including acids, alcohols, and sugar were detected for experiments 1 and 2.

Experiments 1 and 2 can be compared first as no upgrading catalyst was used in those experiments. Hydrogen and nitrogen are supplied at 80:20%. Phenolics are most prominent in both experiments with acids and then ketones. All those functional groups apart from phenolics come from the decomposition of cellulose and hemicellulose whereas phenolics come from the decomposition of lignin[64]. Also, there's a slight difference in weight fraction in each category and it can be noticed that phenolics and furans were increased for experiments with FCC. Similar trends were observed in previous studies and the decrease in phenolics compounds can have a positive impact on the stability of bio-oil as a degree of polymerization reduces with reduction in those compounds.

Ketones were also reduced for FCC experiments and aldehydes and alcohols increased showing its degree of ketonization was less as cracking reactions took place with FCC. Sugar compounds also decreased for FCC as the cracking reactions breaks larger carbon chains and furans and other species increased for it.

Cyclo-oxygenates are highest for (FCC + TiO_2) as compared to all other compounds. It can be noted that using pure titanium dioxide has hydrogenation activity as high as metal catalysts. Phenolics were considerably less than other catalysts showing the conversion of acids, alcohols, and other functional groups into cyclo-oxygenates. From Figure 46, it can be seen that functional groups detected in catalyzed experiments are phenolics, hydrocarbons, cyclo-oxygenates, ketones, and a small number of furans. Cyclo-oxygenates detected in all experiments are primarily ketones which shows the ability of metal oxides to undergo a ketonization reaction pathway to convert lighter molecules to couples and form large species. Although, cyclo-oxygenates are classified separately as HDO pathways can be easily adapted for them. (FCC + TiO_2) > (Sand+ Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2).

Ketonization and aldol reaction mechanisms are predominantly active in the pyrolysis process, particularly with metal-based catalysts on metal oxide supports[65]. It also affects gas formation as discussed in section 8.3. The functional groups like acids, alcohols, and aldehydes were all detected in experiments 1 and 2 showing that smaller chain species are still present and can be converted to longer chain compounds. In a metal-catalyzed reaction, all those species were converted into other species primarily ketones and hydrocarbons along with phenols showing their ability to undergo this pathway. Ketones formed during ketonization reactions serve as an intermediate for aldol condensation reactions which combines smaller chain compounds to form larger chain compounds[66]. Shaolong et. al. studied the ketonization and aldol mechanism on compounds found in pyrolysis crude oil[52]. Figure 47 explains the study of model compounds which serves as the basis for reaction pathways. Hydroxyacetone, a prevalent constituent of crude pyrolysis oil undergoes ketonization and aldol reactions with metal catalysts. It also converts into furans under cyclic reactions. Acetone, which is a common ketonization product continues to form mesityl oxide by reaction with other carbonyls present and continues reaction till closed rings forms[52].

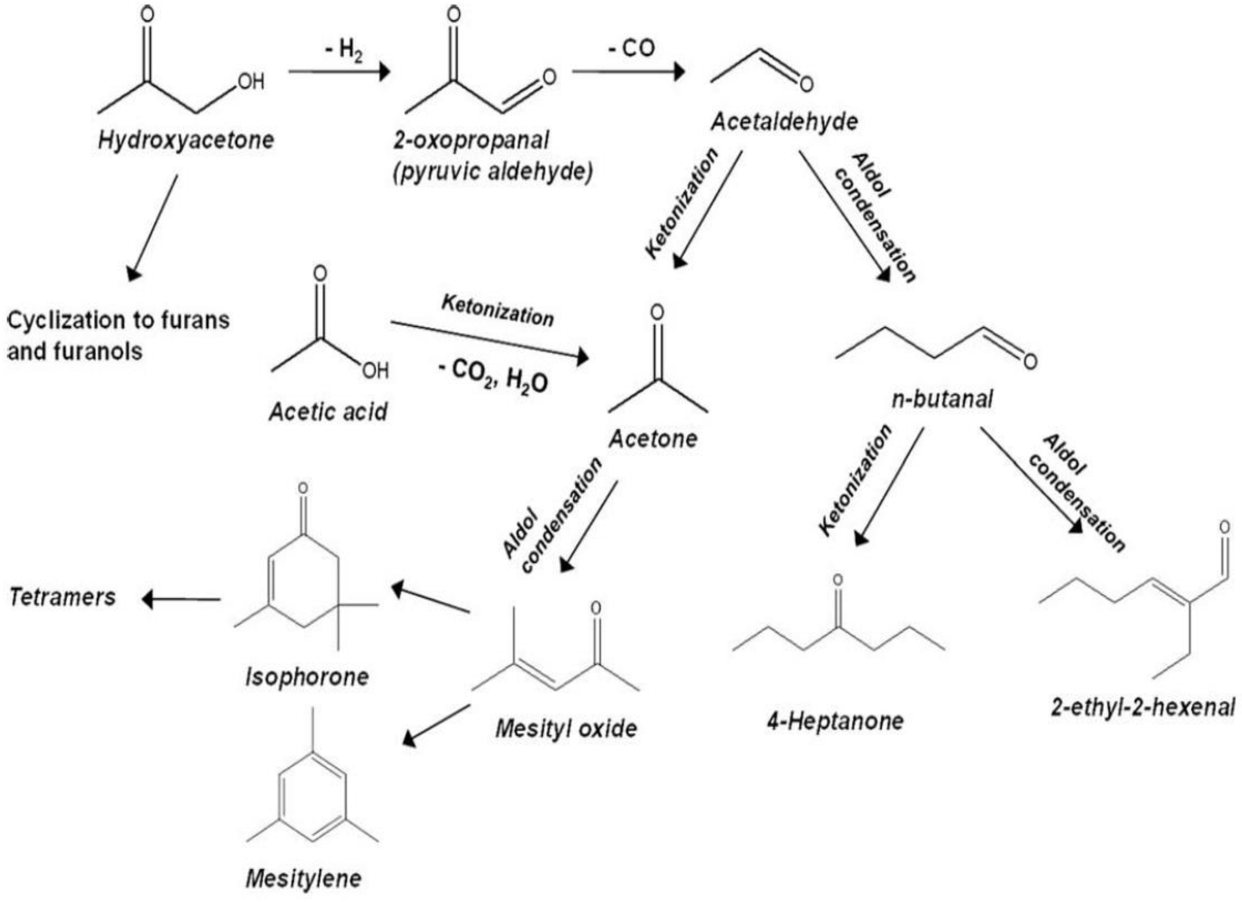


Figure 47: Ketonization and aldol condensation reactions mechanism for hydroxyacetone [52].

Ketones were detected highest for experiment 1 with sand and then (FCC + Ru/TiO_2). It is considerable that (FCC + Co/TiO_2 + Pt/TiO_2) has fewer phenolics and more cyclo-oxygenates along with ketones, as discussed, that cyclo-oxygenates are also ketones with closed rings so including all cyclo-oxygenates and ketones, (FCC + Co/TiO_2 + Pt/TiO_2) has higher ketonization activity. Also (FCC + Co/TiO_2 + Pt/TiO_2) was performed with a higher feed rate and having less residence time has stronger ketonization activity than experiments with less feed rate.

Phenolic compounds are the most abundant functional group detected in catalyzed experiments[64]. Additional reaction pathways that take place with catalysts lead to the formation of phenolic compounds. Mostly alkylated phenolics were detected in a large amount for all catalysts. Phenol, phenol,2-methyl, and phenol,3-methyl were detected in all samples in considerable amounts along with other methyl and ethyl phenols. Phenolics come from the lignin decomposition of biomass and have closed rings, guaiacol a typical constituent of pyrolysis oil produces different compounds in the catalytic pyrolysis process. It has not been detected in any samples and other phenols were founds in the analysis showing they decomposed and reacted completely. Having closed rings, phenols convert directly to aromatics having demethylation and deoxygenation reactions.

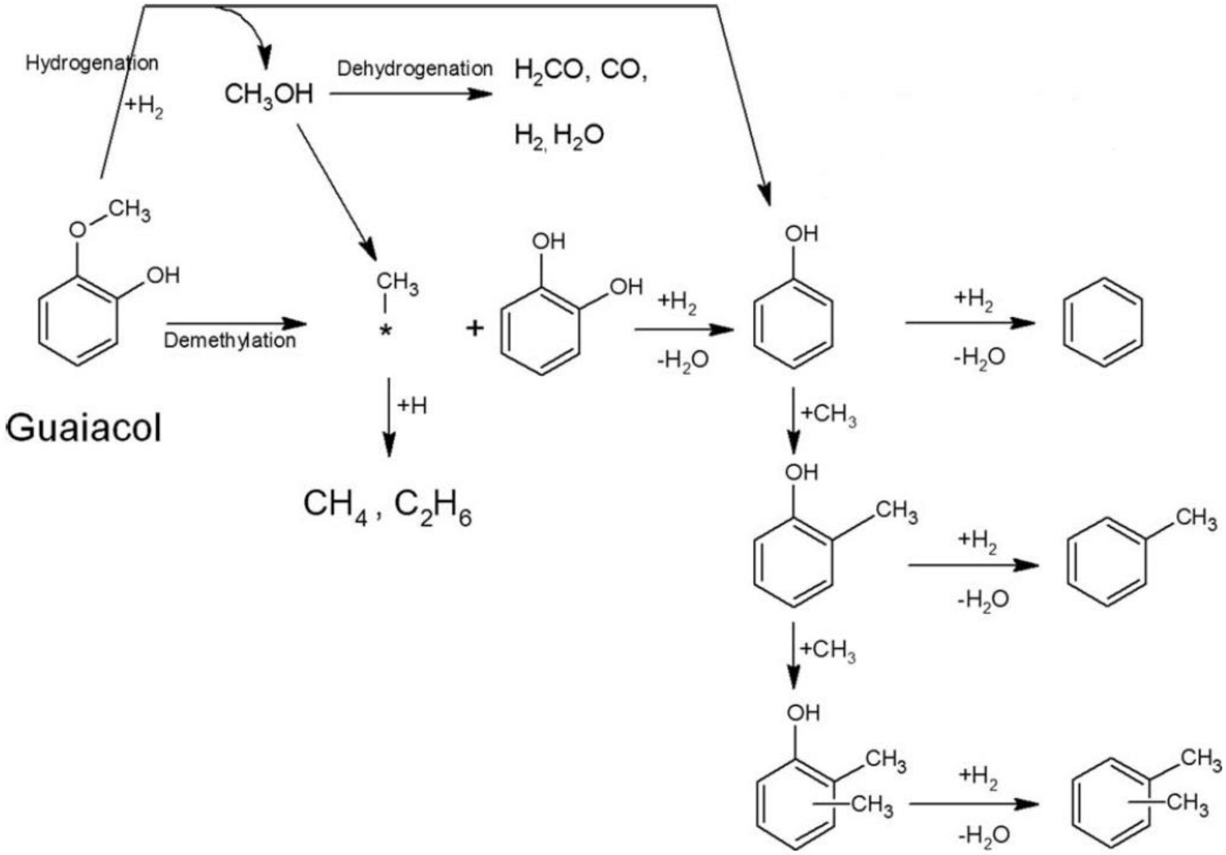


Figure 48: Guaiacol decomposition to aromatics and gases [52].

Methane and ethane are also removed during the breakage of the guaiacol molecule, and the formation of phenol can be seen clearly. Side reactions forming alkylated phenols also take place. Removal of methyl group increases gas phase products as it ends up increasing gas yield.[67] And aromatics also increased for catalyzed reactions showing a reduction in phenols and going to form aromatics with alkylation. There are also some methyl-ethyl phenols detected showing the reactions combined with two alkylation reactions. (FCC + Ru/TiO_2) > (Sand + Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2). (FCC + TiO_2) has considerably fewer phenolics than other catalyzed experiments and a lot of cyclo-oxygenates were identified for it showing the domination of ketonization reactions for it.

Aromatic compounds were found more for (FCC + Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2) > (FCC + TiO_2) > (Sand + Ru/TiO_2). The last two experiments were performed with double feed rate as other experiments it is noted that having less residence time and more feed rate increases aromatics in bio-oil. Also, FCC aiding in aromatization reactions as (Sand + Ru/TiO_2) has less aromatics than other catalyzed reactions showing the additional effect of having FCC as fluidizing medium. As discussed earlier, phenols convert to aromatics directly, the conversion was dependent on the reaction's mechanism having side reactions forming different products which do not increase aromatics but changes bonds formation. HDO reactions with the direct deoxygenation (DDO) pathway give aromatics with the release of water[68].

For all experiments, carbon number analysis was completed to see carbon distribution and functional groups distribution along with carbon distribution. Figure 49 gives carbon distribution based on carbon moles fractions for species identified in the analysis.

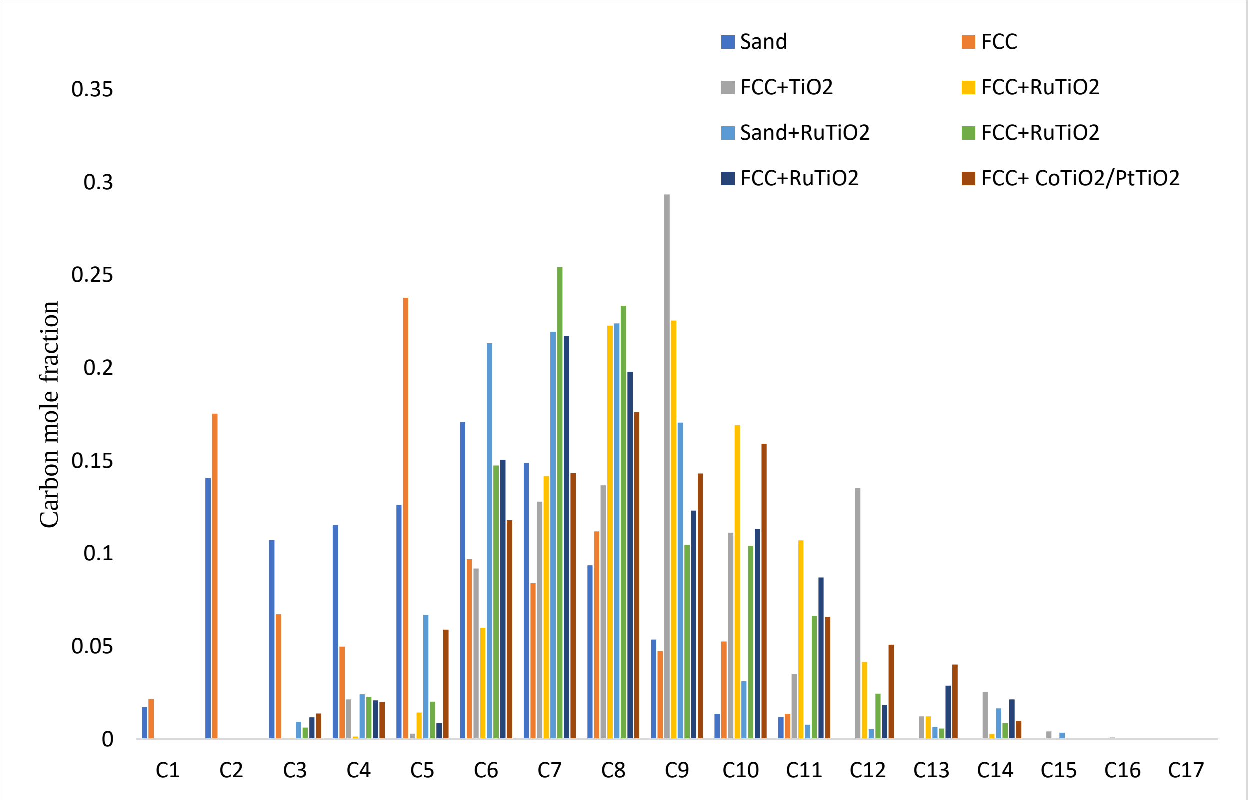


Figure 49: Carbon number analysis for bio-oil samples based on carbon moles.

Sand and FCC experiments have carbon distribution more in the C_1-C_8 range. The presence of smaller chain species was present without any upgrading of bio-oil. It can be estimated that the compounds can be coupled using metal catalysts and upgraded to have more stable bio-oil in a desired carbon length. C-C coupling reactions were taken place with catalyzed experiments as can be seen in Figure 49. As discussed before, the smaller chain species primarily include acids, alcohols, aldehydes, and cyclo-oxygenates which then be converted to either phenols, ketones, and aromatics with metal catalysts. The physical change was also observed for bio-oil samples by observing color change, or viscosity variation having nice flowability. The most prevalent compounds detected with catalyzed experiments were in the range of C_6-C_{12}. Smaller compounds were coupled to form larger chain compounds and more compounds were detected in C_6-C_9 which are phenolics. Phenolics having alkylated groups are distributed in this range. There are compounds detected in the C_{12}-C_{15} range primarily having hydrocarbons. C_{11} does not have hydrocarbons and phenolics were identified for it. Demethylation reactions should be taken place to remove that phenol group that can give aromatics. (FCC + TiO_2) has more C_9 and C_{12} and all are cyclo-oxygenates which shows its ketonization and C-C coupling ability and ketonization reactions.

Functional groups were identified based on carbon number. Ru/TiO_2 was used for multiple experiments to check the catalytic activity for several runs. After running four experiments having almost 50 hours of runtime, the activity of the catalyst was reduced from the first run to the fourth run.

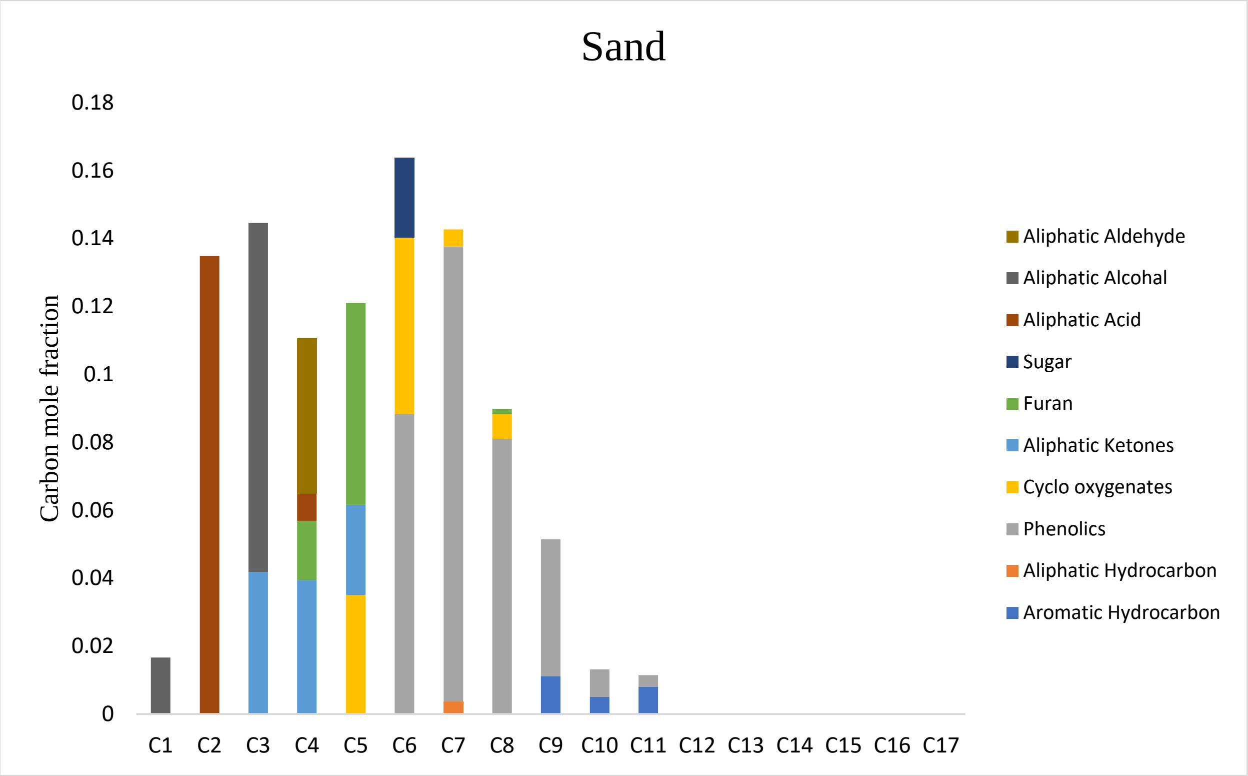


Figure 50: Functional groups based on carbon number for experiment 1.

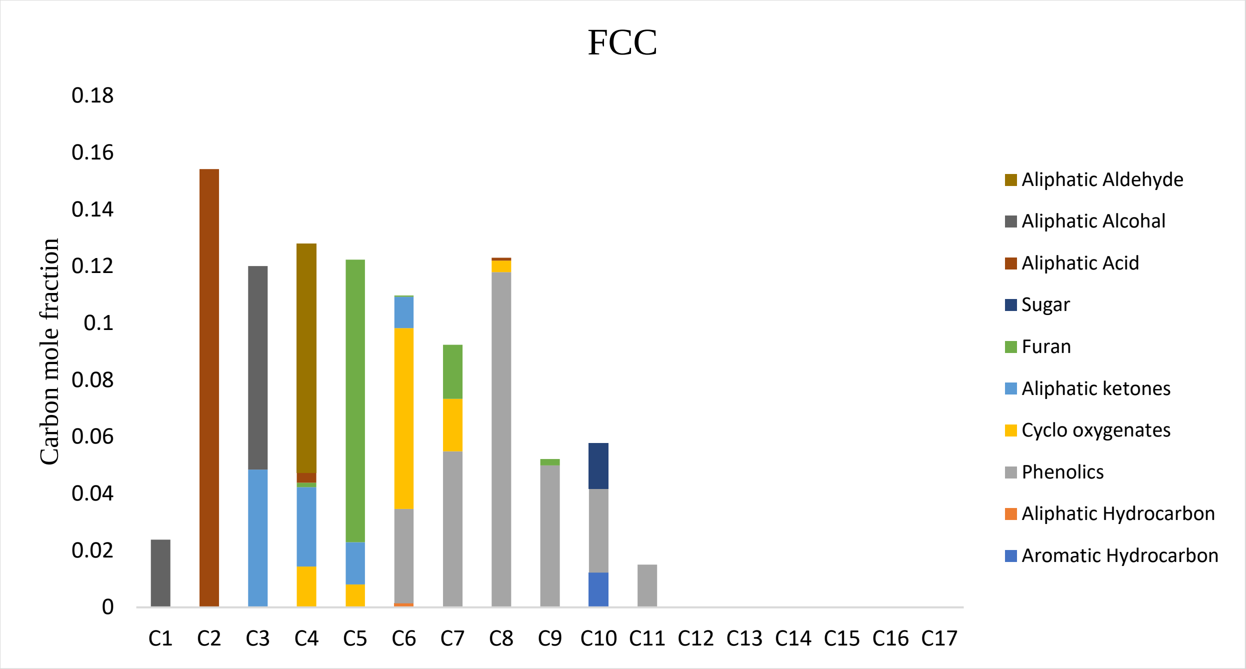


Figure 51: Functional groups based on carbon number for experiment 2.

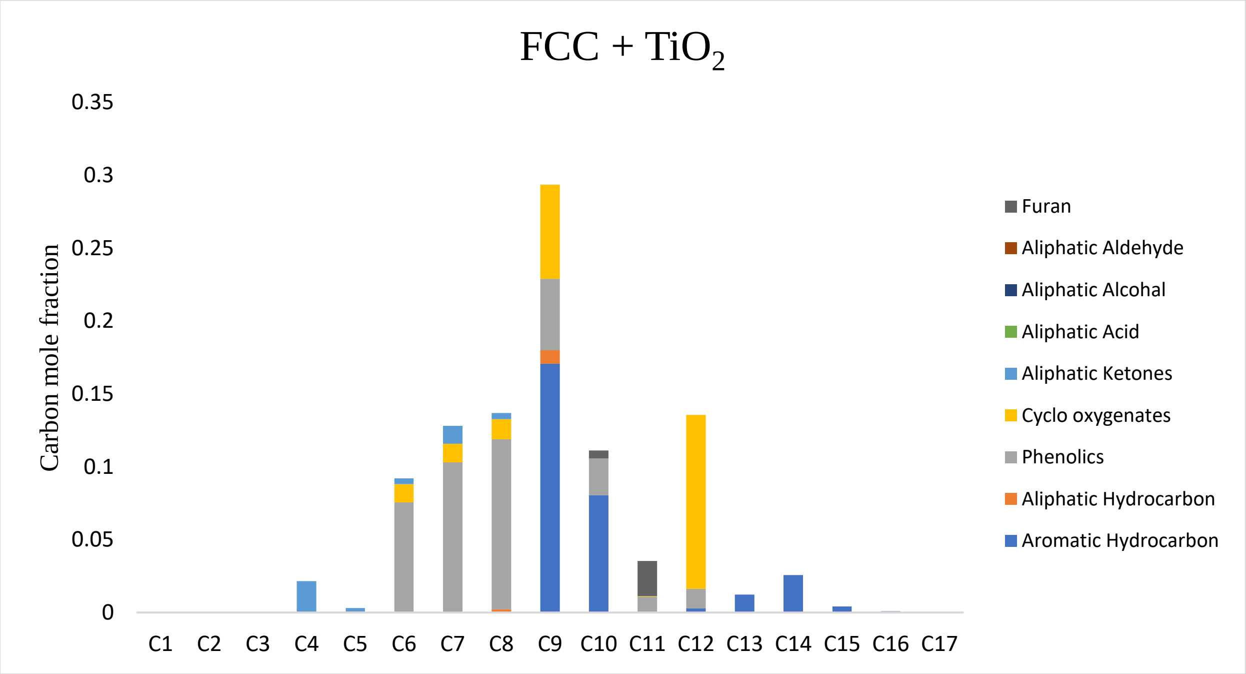


Figure 52: Functional groups based on carbon number for experiment 3.

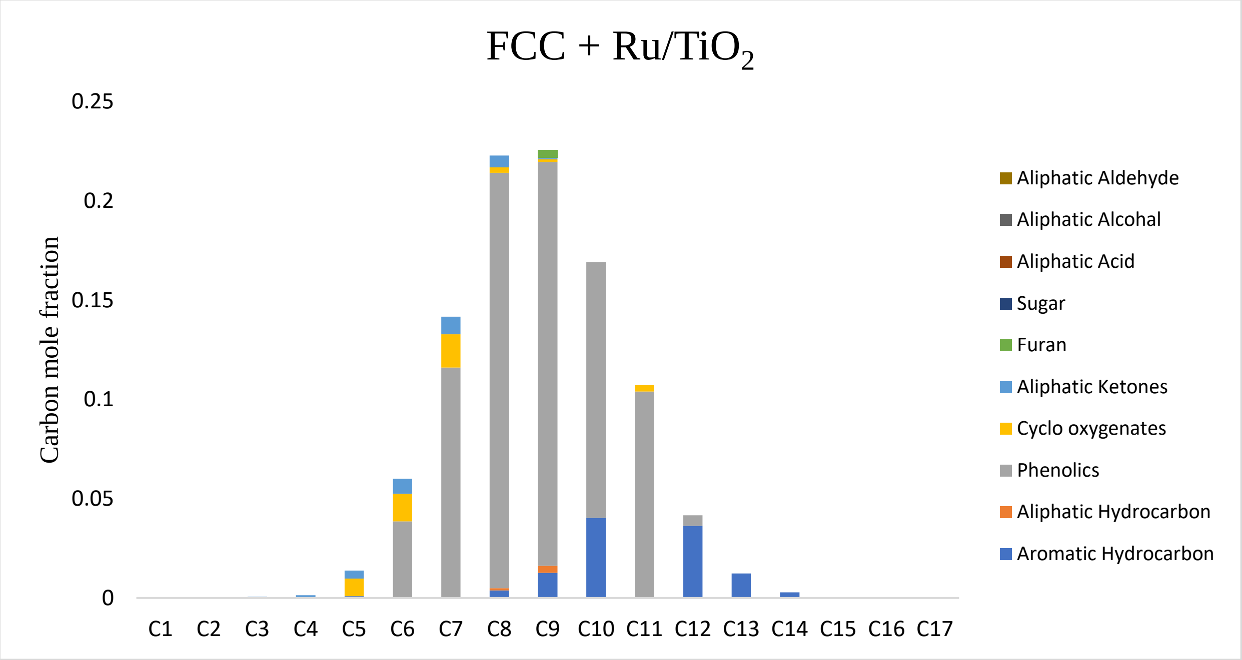


Figure 53: Functional groups based on carbon number for experiment 4.

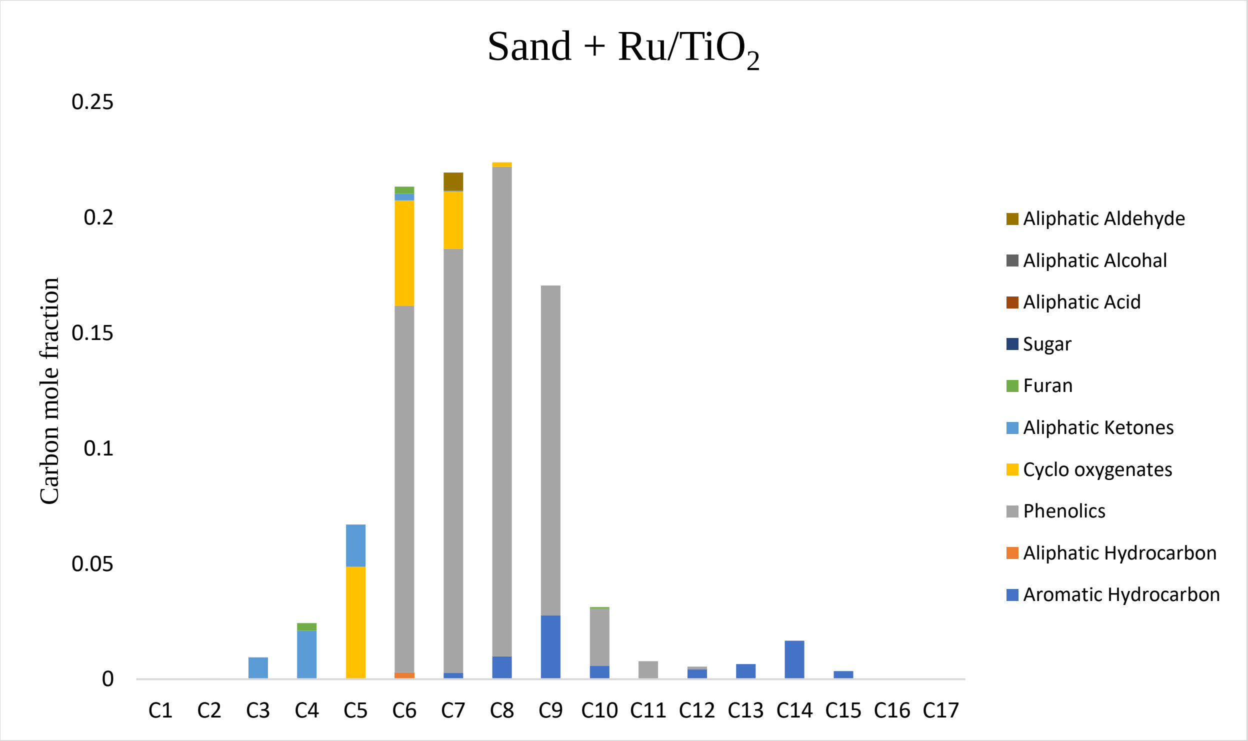


Figure 54: Functional groups based on carbon number for experiment 5.

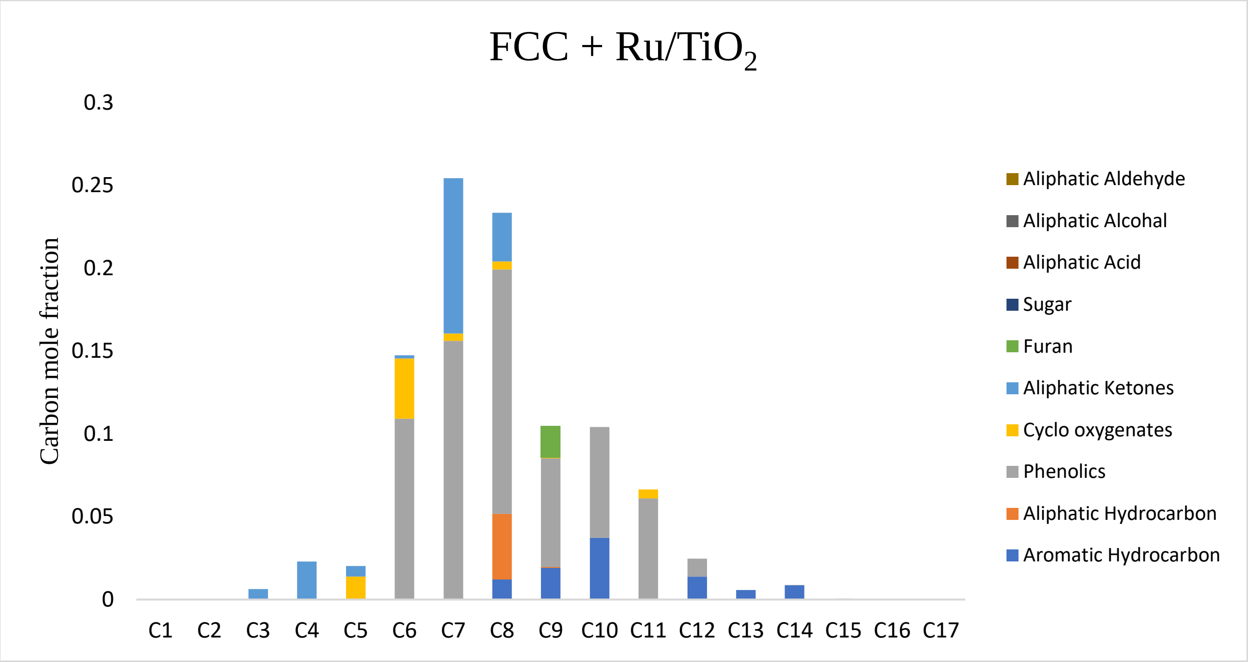


Figure 55: Functional groups based on carbon number for experiment 6.

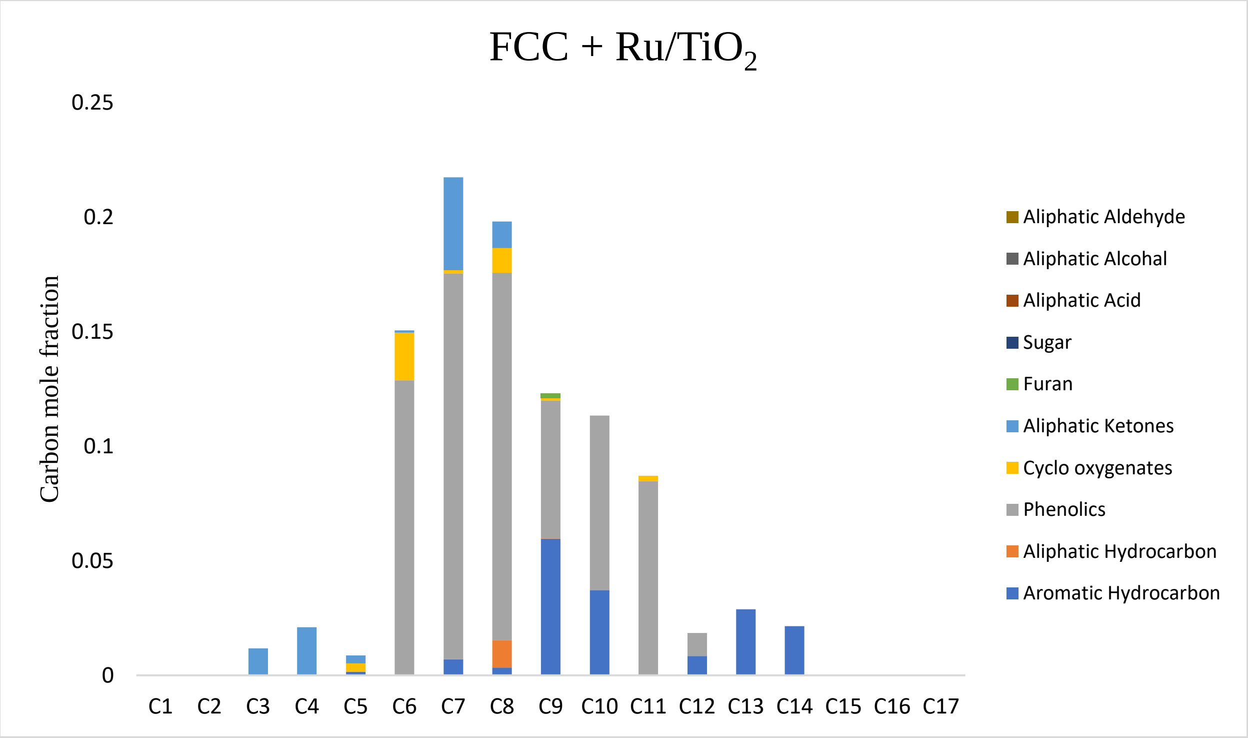


Figure 56: Functional groups based on carbon number for experiment 7.

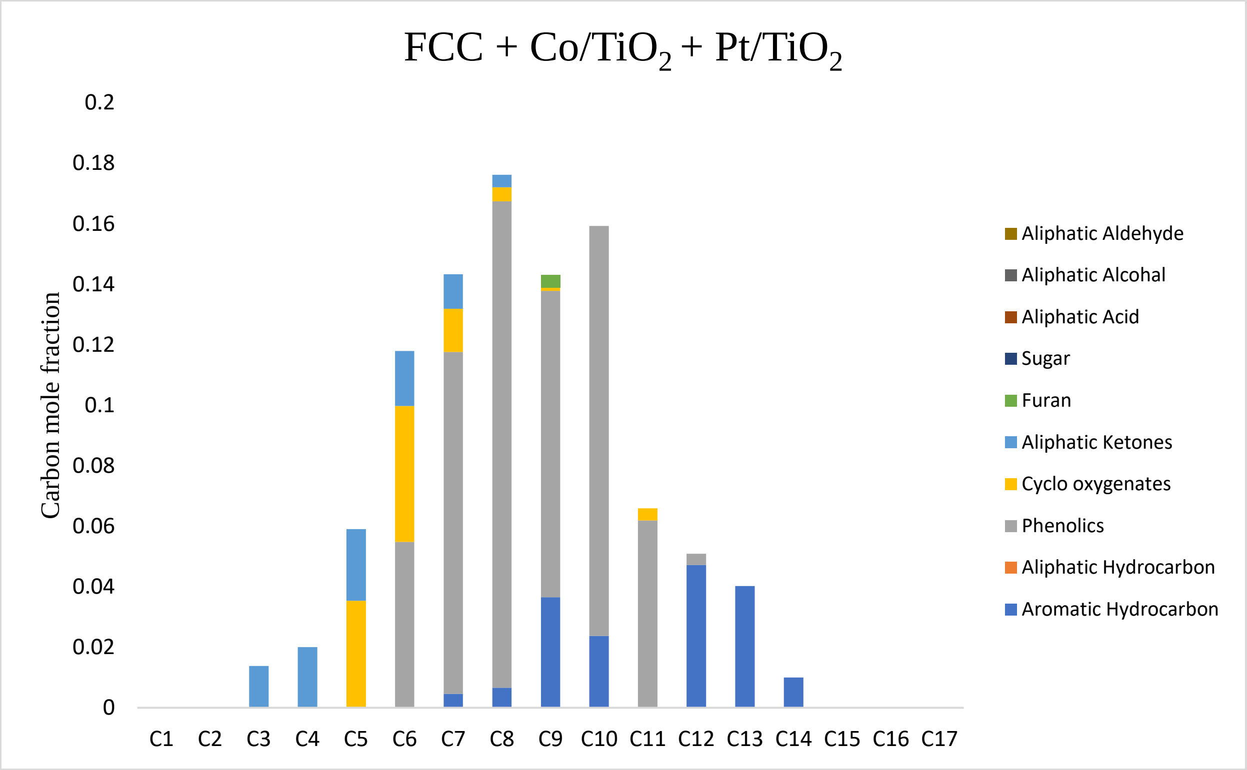


Figure 57: Functional groups based on carbon number for experiment 8.

It can be seen clearly that catalyzed experiments have shifted the carbon lengths towards higher carbon numbers with C-C coupling effects and different functional groups are also identified for each carbon number to see how the reactions going on. Ru/TiO_2 was used for multiple experiments, it can be seen that the compounds with higher carbon length were reduced and the bars were shifted towards the left in the plot showing that after multiple runs the activity of the catalyst was reduced. Coking on the catalyst was also noted which is a major reason for the activity loss as it reduces the pyrolysis vapor's contact with active metal on the catalyst causing limited reactions to occur. It is interesting to note that in the second run, the ketones were increased along with cyclo-oxygenates which can show an increased degree of ketonization. Phenolics along with aromatics decreased. The increase in cyclo-oxygenates also shows closed-ring ketones formation.

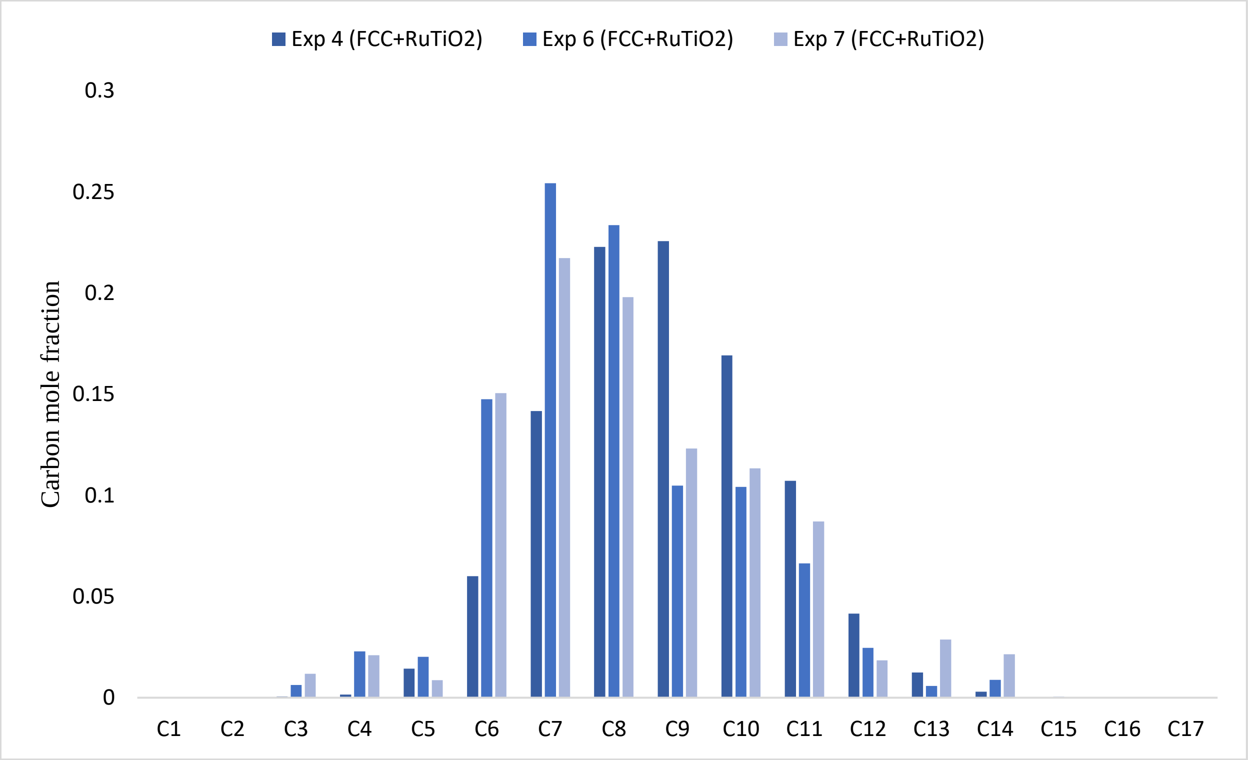


Figure 58: Carbon number analysis for FCC + Ru/TiO_2.

An overall comparison for Ru/TiO_2 is shown in Figure 58. The experiments performed with (FCC + Ru/TiO_2) were compared to having the same process conditions. C_9-C_{12} compounds were high in the first run as can be seen showing the high C-C coupling ability of fresh catalyst. In the other two runs, C_9-C_{12} were reduced considerably, and smaller chain compounds were detected which can show the loss of activity. The increase in C_{13} and C_{14} for a third run can be estimated as it has a double mass feed rate than the second run giving less residence time to start secondary reactions reducing higher phenolics. It can be estimated that after more runs the curves will move towards the extreme left and there will be smaller chain compounds as it is identified in experiments 1 and 2 showing that the catalytic activity is completely lost.

The elemental analysis for carbon, hydrogen, and oxygen which are common constituents of chemical species identified during analysis were compared for experiments with catalysts and without catalysts. It is advantageous to have results analyzed with the same setup to have a more clear idea about the working of the catalysts and their ability to deoxygenation and hydrogen generation is also observed for catalyzed experiments.

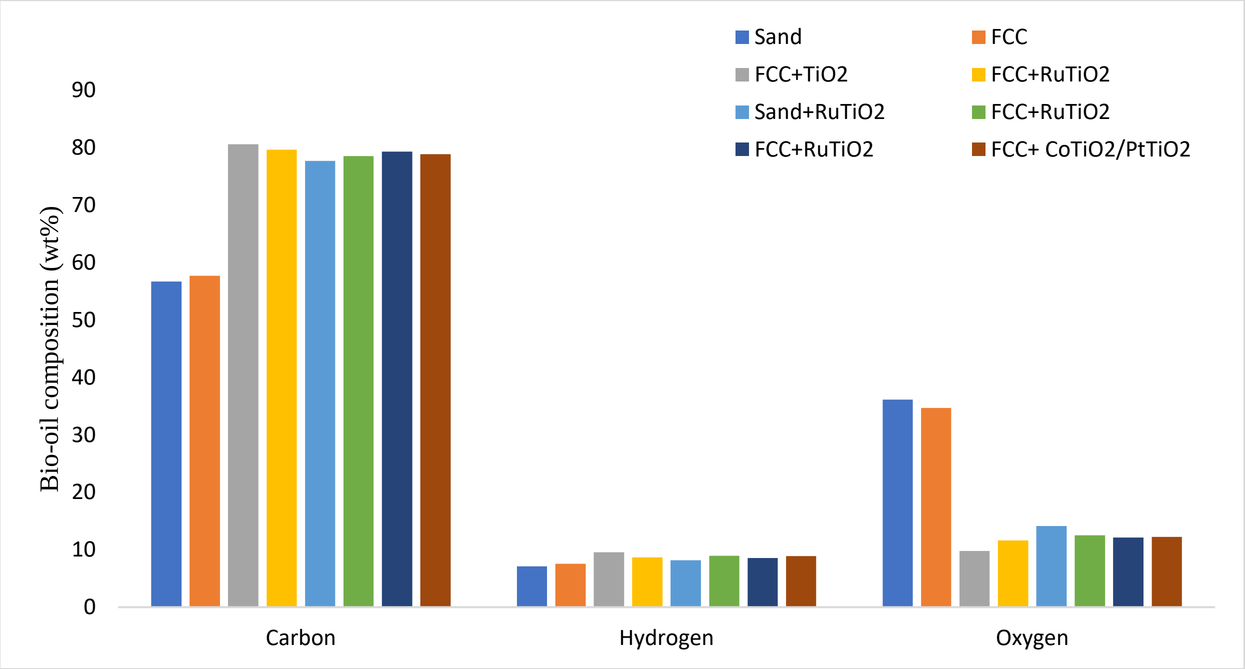


Figure 59: Elemental analysis for bio-oil samples collected.

Without any upgrading catalysts, the experiment with just sand and FCC shows oxygen content around 36 and 34% respectively. A 2% decrease in oxygen percentage shows the activity for FCC taking place and the removal of oxygen occurred. The oxygen content dropped significantly from uncatalyzed to catalyzed experiments. The lowest oxygen content was for (FCC + TiO_2) around 9.8% which is way less than 36%. The highest oxygen content was for (Sand + Ru/ TiO_2) around 14%. All other catalysts have oxygen content in the range of 10-13%. Ru/TiO_2 reduced oxygen content after several runs showing its activity was still present in deoxygenation. Typically, conventional fuels have < 0.05% oxygen content, the inhouse catalysts needed to be tuned to achieve that target but it is important to say that they still reduced oxygen content considerably. 2% difference between (Sand + Ru/ TiO_2) and (FCC + Ru/ TiO_2) showing that FCC aiding in reducing oxygen content.

The hydrogen content was the least for experiment 1 with sand and highest for (FCC + TiO_2). It is observed that with catalyzed experiments hydrogen was increased by around 2%. Hydrogen was supplied for all experiments so it can be estimated that hydrogen was also formed during experiments and it increased the overall yield showing their hydrogenation ability.

Carbon content is the main constituent for conventional fuels and it makes the major part of fuels. (FCC + TiO_2) increased carbon by 80% from 56% which is identified with sand. It is primarily because of the removal of oxygen from bio-oil and increases the carbon yield. It should be noted that 56% is also high for experiment 1 as previous studies found carbon yield around 40% for biomass pyrolysis. The carbon content can be different for different types of biomass. All catalyzed experiments have increased carbon yield by around 80% with (Sand + Ru/ TiO_2) having less carbon yield in comparison to FCC catalysts. From section 4.6, the carbon content in diesel fuel is around 85% which is still more than what is achieved in these experiments. By having more deoxygenation activity, reducing oxygen can lead to fuel range and a more clear overview is explained with the help of van Krevelen diagram. Also, carbon content has a direct impact on the heating value of fuels so increased carbon content increases the heating value of fuels also.

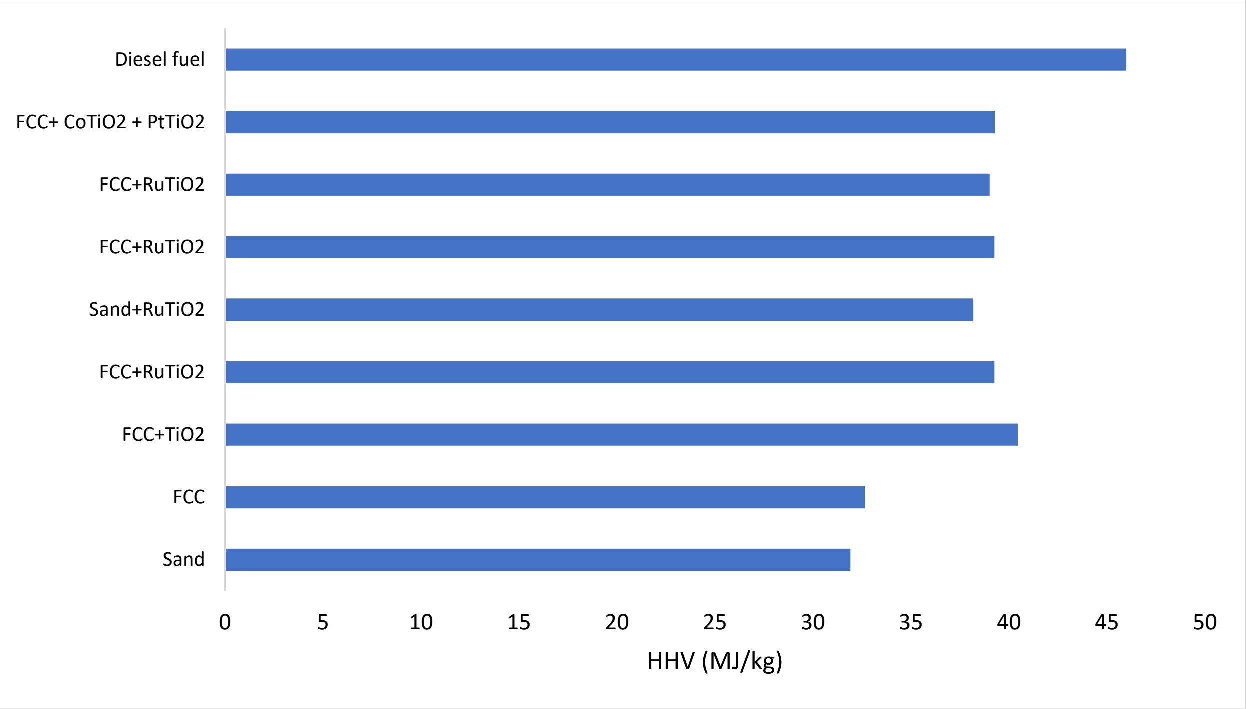


Figure 60: HHV comparison for bio-oil samples and diesel fuel.

Higher heating value (HHV) is estimated to be in direct relation with the carbon composition of the oil and inverse relation to oxygen content. Having more oxygen content reduces the HHV for the fuels. (FCC + TiO_2) has more HHV than other samples analyzed with more carbon content in the bio-oil. Sand and FCC oil samples have significantly less HHV as can be estimated from an elemental analysis that both these samples have around 40% oxygen content as compared to 10% for catalyzed oil samples. The composition of oil is primarily phenolics and removing oxygen content from phenolics at atmospheric pressure with HDO reactions is a bit challenging. The atmospheric pyrolysis process has a good influence on C-C coupling reactions and the influence of deoxygenation for phenolics was hard to achieve at atmospheric pressure. There is still a difference in HHV between diesel fuel and oil samples obtained from experiments noting the difference in composition for carbon and oxygen primarily. Metal oxides have shown great ability in reducing oxygen content from oil samples and different noble metals have already shown good influence in the formation of aromatics. It is all about finding the right metal loading to optimize carbon yield and oxygen removal.

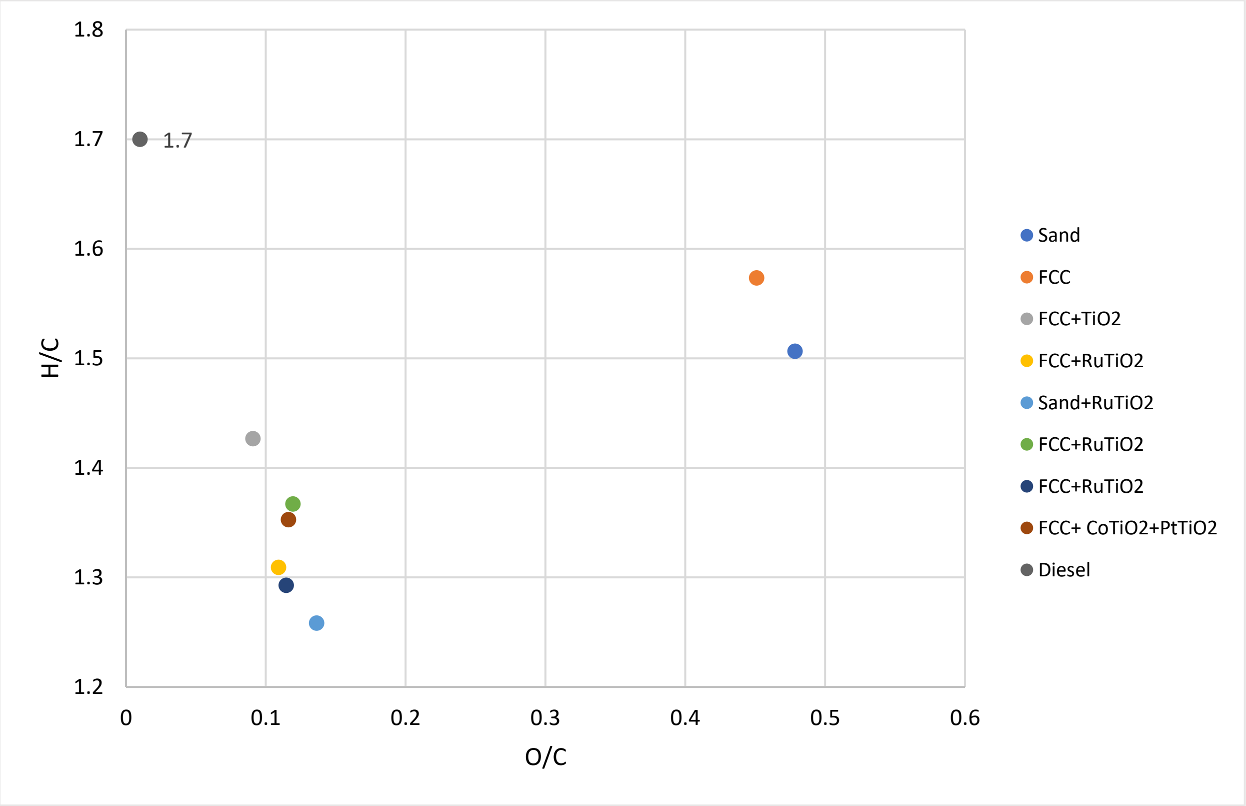


Figure 61: van Krevelen diagram for H/C and O/C ratios comparison.

van Krevelen's diagram in Figure 61 shows a more suitable overview of the elemental analysis done for bio-oil samples obtained from experiments. The fractions are based on moles for the species. Sand and FCC oil samples have higher H/C ratios and more O/C ratios than catalyzed oil samples. FCC oil sample has more H/C ratio than sand giving away hydrogen production during an experiment. Catalyzed experiments have a very close range of H/C ratio with considerably less O/C ratio than uncatalyzed samples, showing that catalysts worked for deoxygenation and hydrogenation as well. There is still some difference between diesel fuel range and bio-oil samples obtained from experiments so having a strong deoxygenation effect of the catalysts will reduce the oxygen content and increases the carbon content in bio-oil and eventually HHV will also improve for bio-oil.

Aqueous phase samples were analyzed for water content as samples were all clear like water. KF titration was done for the analysis and the theory for it is explained in section 5.2 and the procedure to analyze samples was explained in section 7.2.1. Table 13 shows that all samples analyzed have all more than 90% water in them.

Table 13: RI water content for aqueous phase samples

No.	Water content (%)
Experiment 3	94
Experiment4	91
Experiment 5	93
Experiment 6	92
Experiment 7	89
Experiment 8	93

9. Conclusion:

Experiments were performed on pilot plant with catalysts prepared using metal oxide supports. Sand and FCC were used as a fluidizing medium. Titanium dioxide was used as catalyst support for catalysts and pure calcined titanium dioxide was also used to experiment. Physical changes were made to the condensation section, additional condensers were attached to improve the condensation of vapors passing through the primary condenser. The mass yield was increased considerably from 70% to around 90% with bio-oil yield increased from 23 to 34%. The increase in overall mass yield is considerable as documented in the literature for pilot-scale rig at atmospheric pressure. An overall mass yield comparison giving higher to lower mass yield is (Sand + Ru/TiO2) > (FCC + Ru/TiO2) > (FCC + TiO2) > (FCC + Co/TiO2 + Pt/TiO2) > FCC > Sand. All experiments performed with additional condensers have a stable bio-oil mass yield of around 32% which can be improved more with condensation adjustments. The gradual increase in overall mass yield is because additional condensers were attached to the rig after two experiments and also the coolant temperature was reduced to -14^{o}C from -7^{o}C. The gas filter upstream of the upgrading reactor was removed to avoid pressure buildup and a mesh was placed in the pipe connecting two reactors to avoid coking of catalysts by stopping particles passing to the catalysts.

Gases formed during experiments primarily CO, CO_2, CH_4, and lower non-condensable hydrocarbons from C_2-C_6. (FCC + Ru/TiO_2) > (Sand + Ru/TiO_2) > (FCC + Co/TiO_2 + Pt/TiO_2) > (FCC + TiO_2) > FCC > Sand. CO and CO_2 were formed by carbonylation and carboxylation reactions. CO formation is not desired as the removal of oxygen was less than CO_2. Among all experiments performed, (FCC + Co/TiO_2 + Pt/TiO_2) has more CO_2 in the gas phase than CO indicating strong ketonization ability as CO_2 is released during ketonization reactions. C_4-C_6 hydrocarbons. were very less compared to C_2 and C_3 as these two gases were formed as byproducts as well with smaller carbonyls reacting to form larger chain species.

Liquid samples were collected from the primary collection pipe and additional glass condensers were attached to the rig. The first two experiments without upgrading catalysts gave a mixed-phase oil sample, other samples which were obtained by having catalysts had two distinct separate phases. Aqueous phase samples were analyzed for water content and oil samples were analyzed for functional groups present and carbon chain analysis. (FCC + Co/TiO_2 + Pt/TiO_2) has higher ketones yield following (FCC + Ru/TiO_2) showing their ability to undergo ketonization reactions. Aldol condensation reactions also took place simultaneously with ketonization and all smaller carbonyls were completely reacted to form longer chain species. Formation of aromatics also shows aromatization occurred and HDO ability was not prominent to convert phenolics into aromatics.

HHV estimations were also made for all samples along with H/C and O/C ratios showing the advantage of using catalysts to upgrade crude bio-oil. Oxygen content decreased sharply from 40% to 10% and carbon yield increased from 55% to 80% which is good in terms of catalytic activity. Improvements can be made to improve the quality of bio-oil by reducing oxygen and increasing carbon content in bio-oil.

10. Future work:

The experiments were performed with modifications to the existing arrangement and changes made to achieve a higher overall mass yield. The gas filter was removed and the pipe connecting the two reactors can also be used as a mini-tube reactor, an upgrading catalyst can be filled up inside the tube and holders can be placed on both sides. Catalysts tested for upgrading purposes and produced good analysis results. For different catalysts different libraries were made for analysis purposes, it will save a lot of time if one library can be made for all catalysts. Catalysts used had 0.5wt% of metal loading on titanium dioxide support, different metal loading can also be tested to generate results and compare them with already analyzed catalysts. The maximum capacity for a chilling unit is -20^{o}C which can improve the condensation of vapors. As there was freezing occurred during experiments at -14^{o}C as a lot of water was produced during experiments, cooling water above 0^{o}C should be used for the primary condenser, and additional condensers -20^{o}C can be set for the chilling unit to condense more vapors increasing mass yield. Non-catalytic experiments should be performed with every new process condition at the same rig to have accurate comparison instead of using data from literature and sold products can also be analyzed using TGA to get information about the composition of coke and char.

References:

1. Initiative, T.S.S., *Availability of Sustainable Fuels*. 2021.
2. Forum, W.E. *Norway new cars sales*. 2021; Available from: https://www.weforum.org/agenda/2021/01/electric-cars-record-market-share-norway-2020.
3. Thomas Hundertmark, M.M., *How plastics waste recycling could transform the chemical industry*. 2018.
4. Jha, S., et al., *A review of thermochemical conversion of waste biomass to biofuels.* Energies, 2022. **15**(17): p. 6352.
5. Agency, I.E. *Global EV Data* 2022; Available from: https://www.iea.org/data-and-statistics/data-tools/global-ev-data-explorer.
6. Organization, W.B., *GLOBAL BIOMASS POTENTIAL TOWARDS 2035*. 2015.
7. Haarlemmer, G., et al., *Analysis and comparison of bio-oils obtained by hydrothermal liquefaction and fast pyrolysis of beech wood.* Fuel, 2016. **174**: p. 180-188.
8. Gucho, E.M., et al., *Experimental study on dry torrefaction of beech wood and miscanthus.* Energies, 2015. **8**(5): p. 3903-3923.
9. Behrendt, F., et al., *Direct liquefaction of biomass.* Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology, 2008. **31**(5): p. 667-677.
10. Zhang, S., et al., *Liquefaction of biomass and upgrading of bio-oil: a review*. Molecules, 2019. **24**(12): p. 2250.
11. Yakaboylu, O., et al., *Supercritical water gasification of biomass: a literature and technology overview*. Energies, 2015. **8**(2): p. 859-894.

12. Situmorang, Y.A., et al., *Steam gasification of co-pyrolysis chars from various types of biomass.* International Journal of Hydrogen Energy, 2021. **46**(5): p. 3640-3650.

13. Elliott, D.C., *Catalytic hydrothermal gasification of biomass.* Biofuels, Bioproducts and Biorefining, 2008. **2**(3): p. 254-265.

14. Bridgwater, A.V., D. Meier, and D. Radlein, *An overview of fast pyrolysis of biomass.* Organic geochemistry, 1999. **30**(12): p. 1479-1493.

15. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading.* Biomass and bioenergy, 2012. **38**: p. 68-94.

16. Bridgwater, T., *Challenges and opportunities in fast pyrolysis of biomass: Part I.* Johnson Matthey Technology Review, 2018. **62**(1): p. 118-130.

17. Osman, A.I., et al., *Conversion of biomass to biofuels and life cycle assessment: a review.* Environmental chemistry letters, 2021. **19**: p. 4075-4118.

18. Balat, M., *Biomass energy and biochemical conversion processing for fuels and chemicals.* Energy Sources, Part A, 2006. **28**(6): p. 517-525.

19. Dabros, T.M., et al., *Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis.* Progress in Energy and Combustion Science, 2018. **68**: p. 268-309.

20. Stummann, M.Z., et al., *A perspective on catalytic hydropyrolysis of biomass.* Renewable and Sustainable Energy Reviews, 2021. **143**: p. 110960.

21. Resende, F.L., *Recent advances on fast hydropyrolysis of biomass.* Catalysis Today, 2016. **269**: p. 148-155.

22. Oh, S., et al., *Fast hydropyrolysis of biomass Conversion: A comparative review.* Bioresource technology, 2021. **342**: p. 126067.

23. Fréty, R., et al., *Cracking and hydrocracking of triglycerides for renewable liquid fuels: alternative processes to transesterification.* Journal of the Brazilian Chemical Society, 2011. **22**: p. 1206-1220.

24. Lee, H., et al., *Recent advances in the catalytic hydrodeoxygenation of bio-oil.* Korean Journal of Chemical Engineering, 2016. **33**: p. 3299-3315.

25. Ma, Q., et al., *Alkylation of phenol: a mechanistic view.* The Journal of Physical Chemistry A, 2006. **110**(6): p. 2246-2252.

26. Dayton, D.C., et al., *Biomass hydropyrolysis in a pressurized fluidized bed reactor.* Energy & fuels, 2013. **27**(7): p. 3778-3785.

27. Meesuk, S., et al., *Fast pyrolysis of rice husk in a fluidized bed: effects of the gas atmosphere and catalyst on bio-oil with a relatively low content of oxygen.* Energy & Fuels, 2011. **25**(9): p. 4113-4121.

28. He, Y., et al., *Comparative study of fast pyrolysis, hydropyrolysis and catalytic hydropyrolysis of poplar sawdust and rice husk in a modified Py-GC/MS microreactor system: Insights into product distribution, quantum description and reaction mechanism.* Renewable and Sustainable Energy Reviews, 2020. **119**: p. 109604.

29. Marker, T.L., et al., *Integrated hydropyrolysis and hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, part 1: Proof of principle testing.* Environmental Progress & Sustainable Energy, 2012. **31**(2): p. 191-199.

30. Marker, T.L., et al., *Integrated hydropyrolysis and hydroconversion (IH2®) for the direct production of gasoline and diesel fuels or blending components from biomass, Part 2:*

continuous testing. Environmental Progress & Sustainable Energy, 2014. **33**(3): p. 762-768.

31. Sadeghbeigi, R., *Fluid catalytic cracking handbook: design, operation, and troubleshooting of FCC facilities*. 2000: Gulf.

32. Trendewicz, A., et al., *One dimensional steady-state circulating fluidized-bed reactor model for biomass fast pyrolysis.* Fuel, 2014. **133**: p. 253-262.

33. Dutta, A., et al., *Conceptual process design and techno-economic assessment of ex situ catalytic fast pyrolysis of biomass: A fixed bed reactor implementation scenario for future feasibility*. Topics in Catalysis, 2016. **59**: p. 2-18.

34. Stummann, M.Z., et al., *New insights into the effect of pressure on catalytic hydropyrolysis of biomass.* Fuel Processing Technology, 2019. **193**: p. 392-403.

35. M. Z. Stummann, A.D.J., *Catalytic hydropyrolysis for sustainable aviation fuel*

36. Melligan, F., et al., *Hydro-pyrolysis of biomass and online catalytic vapor upgrading with Ni-ZSM-5 and Ni-MCM-41*. Energy & Fuels, 2012. **26**(10): p. 6080-6090.

37. Dayton, D.C., et al., *Biomass hydropyrolysis in a fluidized bed reactor.* Energy & Fuels, 2016. **30**(6): p. 4879-4887.

38. Ahamed, T.S., et al., *Upgrading of bio-oil from thermochemical conversion of various biomass–Mechanism, challenges and opportunities.* Fuel, 2021. **287**: p. 119329.

39. Gea, S., et al., *Bio-oil hydrodeoxygenation over zeolite-based catalyst: the effect of zeolite activation and nickel loading on product characteristics.* International Journal of Energy and Environmental Engineering, 2022. **13**(2): p. 541-553.

40. Zupko, R., *Life cycle assessment of the production of gasoline and diesel from forest residues using integrated hydropyrolysis and hydroconversion.* The International Journal of Life Cycle Assessment, 2019. **24**: p. 1793-1804.

41. Mastral, A., et al., *Influence of process variables on oils from tire pyrolysis and hydropyrolysis in a swept fixed bed reactor.* Energy & Fuels, 2000. **14**(4): p. 739-744.

42. Canel, M., Z. Mısırlıogˇlu, and A. Sınagˇ, *Hydropyrolysis of a Turkish lignite (Tunçbilek) and effect of temperature and pressure on product distribution.* Energy Conversion and Management, 2005. **46**(13-14): p. 2185-2197.

43. Venkatesan, K., et al., *Evaluation of pressure and temperature effects on hydropyrolysis of pine sawdust: pyrolysate composition and kinetics studies.* Reaction Chemistry & Engineering, 2020. **5**(8): p. 1484-1500.

44. Abnisa, F. and W.M.A.W. Daud, *A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil.* Energy Conversion and Management, 2014. **87**: p. 71-85.

45. Venkatakrishnan, V.K., et al., *High-pressure fast-pyrolysis, fast-hydropyrolysis and catalytic hydrodeoxygenation of cellulose: production of liquid fuel from biomass.* Green Chemistry, 2014. **16**(2): p. 792-802.

46. Scholz, E., *Karl Fischer titration: determination of water*. 2012: Springer Science & Business Media.

47. Chorkendorff, I. and J.W. Niemantsverdriet, *Concepts of modern catalysis and kinetics*. 2017: John Wiley & Sons.

48. Matter, P.H., et al., *Oxygen reduction reaction catalysts prepared from acetonitrile pyrolysis over alumina-supported metal particles.* The Journal of Physical Chemistry B, 2006. **110**(37): p. 18374-18384.

49. Bankmann, M., et al., *Forming of high surface area TiO2 to catalyst supports.* Catalysis Today, 1992. **14**(2): p. 225-242.

50. Shu, R., et al., *Efficient catalytic hydrodeoxygenation of phenolic compounds and bio-oil over highly dispersed Ru/TiO2.* Fuel Processing Technology, 2019. **184**: p. 12-18.

51. Shi, Y., et al., *Recent progress on upgrading of bio-oil to hydrocarbons over metal/zeolite bifunctional catalysts.* Catalysis Science & Technology, 2017. **7**(12): p. 2385-2415.

52. Wan, S., et al., *Direct catalytic upgrading of biomass pyrolysis vapors by a dual function Ru/TiO2 catalyst.* AIChE Journal, 2013. **59**(7): p. 2275-2285.

53. Eschenbacher, A., et al., *Enhancing bio-oil quality and energy recovery by atmospheric hydrodeoxygenation of wheat straw pyrolysis vapors using Pt and Mo-based catalysts.* Sustainable Energy & Fuels, 2020. **4**(4): p. 1991-2008.

54. Zhang, H., et al., *Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized catalytic cracking (FCC) catalysts.* Energy & Fuels, 2009. **23**(12): p. 6199-6206.

55. Mohammed, A. and A. Abdullah. *Scanning electron microscopy (SEM): A review*. in *Proceedings of the 2018 International Conference on Hydraulics and Pneumatics—HERVEX, Băile Govora, Romania*. 2018.

56. Restoration, C.C.f.B.a.E. *The Transmission Electron Microscope*. Available from: https://www.ccber.ucsb.edu/ucsb-natural-history-collections-botanical-plant-anatomy/transmission-electron-microscope.

57. Nasrollahzadeh, M., et al., *Plant-mediated green synthesis of nanostructures: mechanisms, characterization, and applications*, in *Interface science and technology*. 2019, Elsevier. p. 199-322.

58. Epp, J., *X-ray diffraction (XRD) techniques for materials characterization*, in *Materials characterization using nondestructive evaluation (NDE) methods*. 2016, Elsevier. p. 81-124.

59. Králik, M., *Adsorption, chemisorption, and catalysis.* Chemical Papers, 2014. **68**(12): p. 1625-1638.

60. Pinna, F., *Supported metal catalysts preparation.* Catalysis Today, 1998. **41**(1-3): p. 129-137.

61. Wan, H., R.V. Chaudhari, and B. Subramaniam, *Aqueous phase hydrogenation of acetic acid and its promotional effect on p-cresol hydrodeoxygenation.* Energy & fuels, 2013. **27**(1): p. 487-493.

62. Jahromi, H. and F. Agblevor, *Hydrodeoxygenation of Acetic Acid As a Model Compound for the Aqueous Phase Catalytic Pyrolysis Oils.* 2017.

63. Gopeesingh, J., et al., *Kinetic and Mechanistic Analysis of the Hydrodeoxygenation of Propanoic Acid on Pt/SiO2.* Industrial & Engineering Chemistry Research, 2021. **60**(45): p. 16171-16187.

64. Zheng, Y., et al., *Advanced catalytic upgrading of biomass pyrolysis vapor to bio-aromatics hydrocarbon: A review.* Applications in Energy and Combustion Science, 2022. **10**: p. 100061.

65. Pham, T.N., D. Shi, and D.E. Resasco, *Reaction kinetics and mechanism of ketonization of aliphatic carboxylic acids with different carbon chain lengths over Ru/TiO2 catalyst.* Journal of catalysis, 2014. **314**: p. 149-158.

66. Chheda, J.N. and J.A. Dumesic, *An overview of dehydration, aldol-condensation and hydrogenation processes for production of liquid alkanes from biomass-derived carbohydrates.* Catalysis Today, 2007. **123**(1-4): p. 59-70.

67. Huang, J., et al., *Theoretical studies on pyrolysis mechanism of guaiacol as lignin model compound.* Journal of renewable and sustainable energy, 2013. **5**(4).

68. Dai, L., et al., *A review on selective production of value-added chemicals via catalytic pyrolysis of lignocellulosic biomass.* Science of the Total Environment, 2020. **749**: p. 142386.

Appendix:

Gas phase calculations:

The table below shows the wt.% of gases analyzed by GC TCD for all experiments. The peak area recorded from GC TCD/FID is used to get the individual mass flow of each gas. The calculation for FID analysis based on CH_4 and N_2 was used as a reference for other component calculations. An analogy to calculate the flow rate is given below:

$$\mathrm{n_{C5}} = \frac{\mathrm{n_{CH_4}} \times \mathrm{A_{pentane}}}{\mathrm{A_{CH_4}} \times 5}$$

The molar flow is then converted to the mass flow rate:

$$\mathrm{m_{C5}} = \mathrm{n_{C5}} \times \mathrm{M_{C5}}$$

And the mass is calculated by dividing the mass flow rate by time interval:

$$\mathrm{mass} = \frac{\mathrm{m_{C5}}}{\mathrm{time}}$$

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
CO	7.67%	9.02%	10.68%	11.28%
CO_2	7.17%	5.49%	7.74%	10.19%
CH_4	1.57%	1.85%	2.04%	2.57%
C_2	0.28%	0.42%	0.84%	1.08%
C_3	0.38%	0.53%	1.74%	1.73%
C_4	0.49%	0.68%	0.54%	0.59%
C_5	0.33%	1.92%	0.51%	0.81%
C_6	0.14%	0.29%	0.30%	0.59%

	Experiment 5	Experiment 6	Experiment 7	Experiment 8
CO	13.57%	10.46%	18.36%	8.41%
CO_2	12.33%	6.94%	8.41%	12.88%
CH_4	3.55%	2.11%	3.91%	2.42%
C_2	1.36%	0.86%	1.82%	1.10%
C_3	1.23%	0.69%	1.14%	1.68%
C_4	0.69%	0.62%	0.74%	0.65%
C_5	1.26%	0.68%	0.59%	0.78%
C_6	0.66%	0.28%	0.28%	0.66%

Liquid phase calculations:

The table below shows the selectivity (wt %) of the compounds analyzed in the aqueous phase of bio-oil. The peak area for DCM from GC FID was used as a reference to find the chemical area for all compounds and is given by:

$$\mathrm{y}_{\text{Chemical area}} = \frac{\mathrm{y}_{\text{FID area}}}{\text{DCM area}}$$

where y is a chemical compound.

The weight of compounds is calculated as:

$$\mathrm{wt}_{\mathrm{y}} = \mathrm{RRF} \times \mathrm{y}_{\text{Chemical area}} \times \mathrm{wt}_{\mathrm{DCM}}$$

where RRF is the response factor.

The weight fraction is:

$$\mathrm{wt}_{\mathrm{fr}} = \frac{\mathrm{wt}_{\mathrm{y}}}{\text{total wt}}$$

Actual weight is calculated by:

$$\text{Actual weight} = \mathrm{wt}_{\mathrm{fr}} \times \mathrm{wt}_{\text{dry oil}}$$

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Aromatic Hydrocarbon	0.02	0.01	0.12	0.09
Aliphatic Hydrocarbon	0.00	0.00	0.01	0.00
Phenolics	0.29	0.24	0.41	0.82
Cyclo oxygenates	0.09	0.09	0.38	0.05
Aliphatic ketones	0.19	0.13	0.05	0.03
Aliphatic acids	0.20	0.22	0.00	0.00
Aliphatic alcohols	0.05	0.07	0.00	0.00
Aliphatic aldehydes	0.05	0.08	0.00	0.00
Furan derivative	0.07	0.11	0.03	0.00
Sugar	0.03	0.01	0.00	0.00

	Experiment 5	Experiment 6	Experiment 7	Experiment 8
Aromatic Hydrocarbon	0.06	0.08	0.15	0.15
Aliphatic Hydrocarbon	0.01	0.04	0.01	0.00
Phenolics	0.73	0.62	0.70	0.63
Cyclo oxygenates	0.13	0.07	0.04	0.11
Aliphatic ketones	0.06	0.18	0.10	0.10
Aliphatic acids	0.00	0.00	0.00	0.00
Aliphatic alcohols	0.00	0.00	0.00	0.00
Aliphatic aldehydes	0.01	0.00	0.00	0.00
Furan derivative	0.01	0.02	0.00	0.00
Sugar	0.00	0.00	0.00	0.00

The water content for experiment 3 sample from KF titration is calculated:

$$\text{RI content} = 2.66378\%$$

The dilution factor is calculated as:

$$\text{Dilution factor} = \frac{22.9325}{0.642}$$

Water content is:

$$\text{water content (\%)} = \text{RI content } \times \text{dilution factor}$$

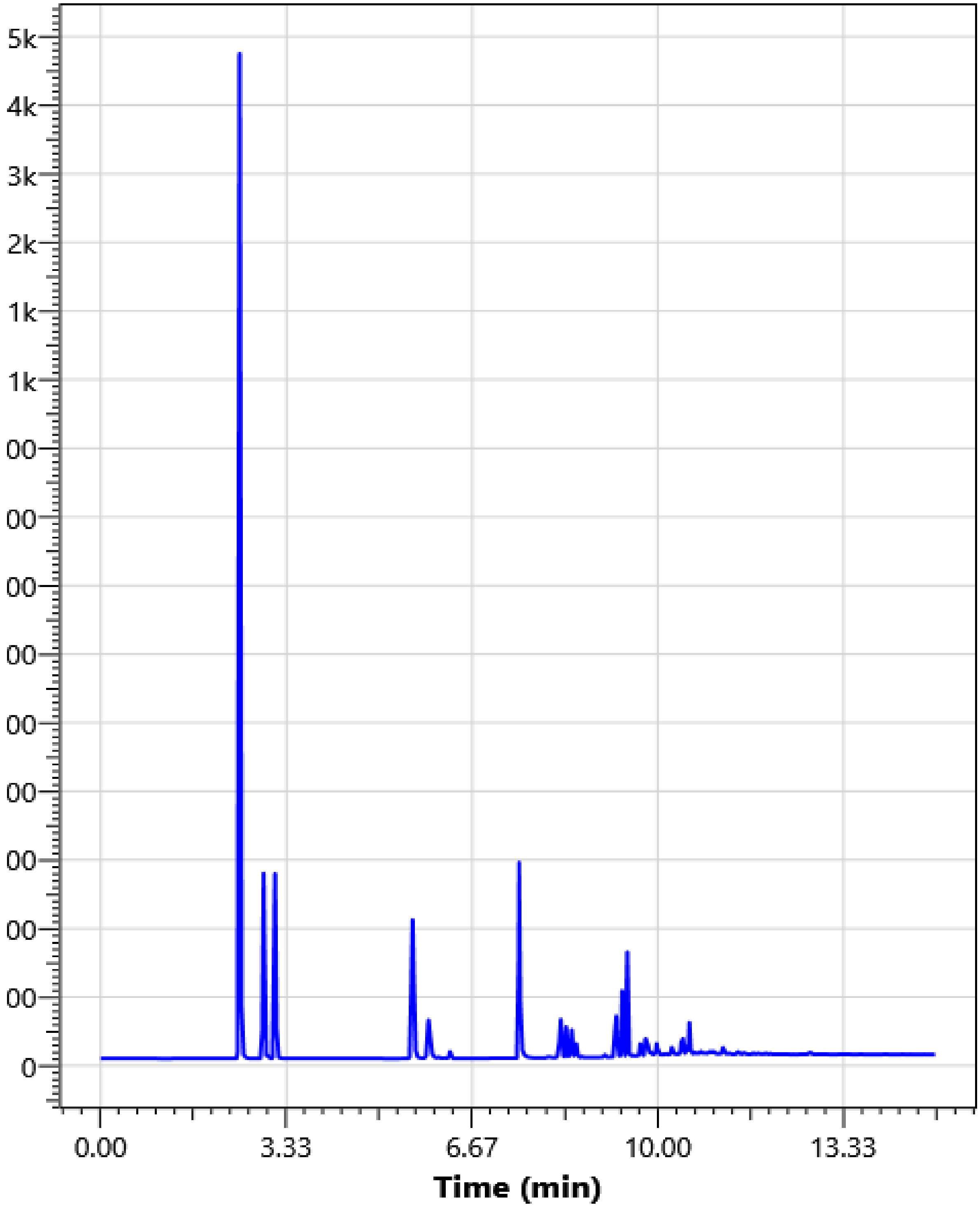
$$\text{water content (\%)} = 94.3\%$$

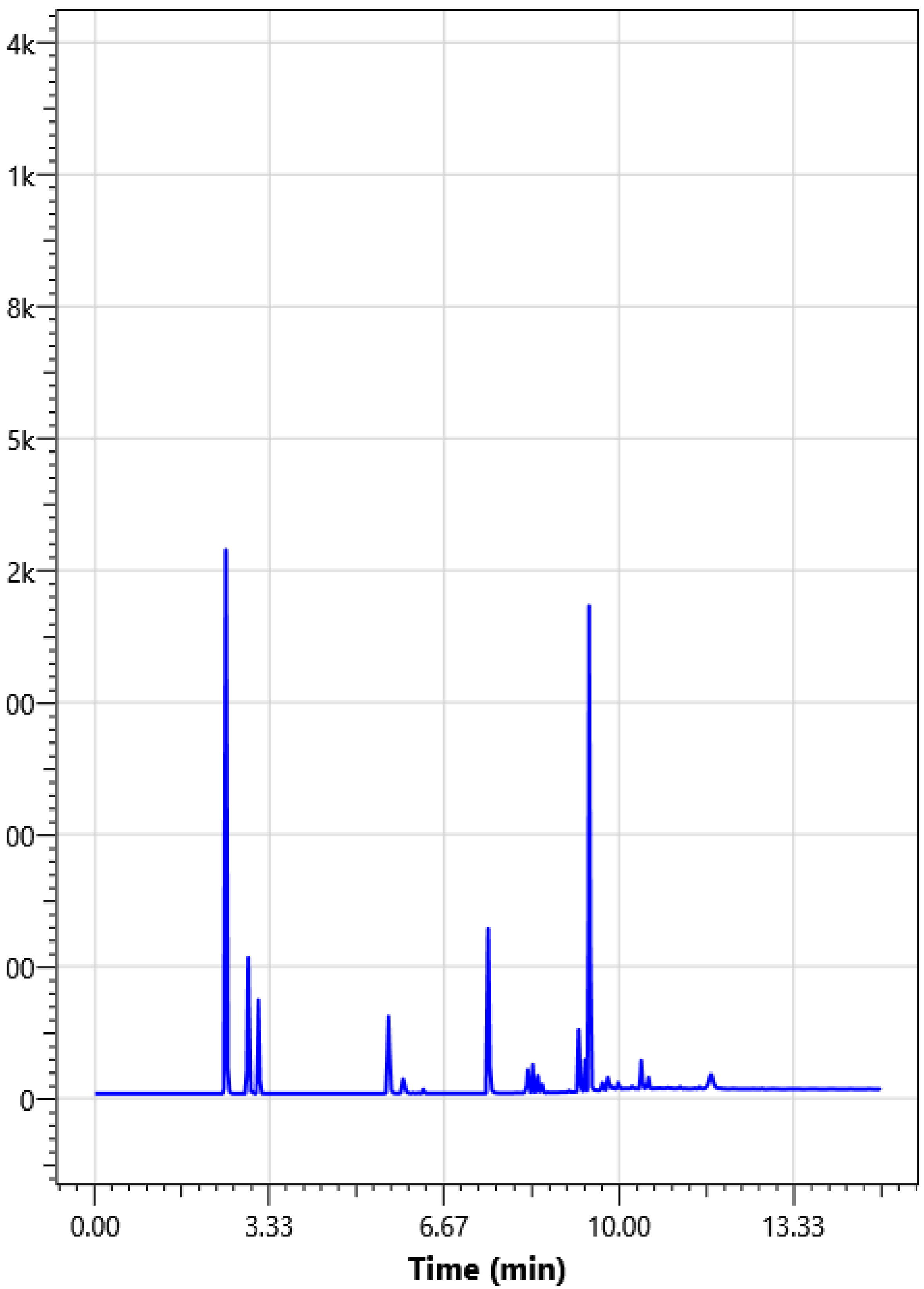
Higher heating value is calculated using the equation:

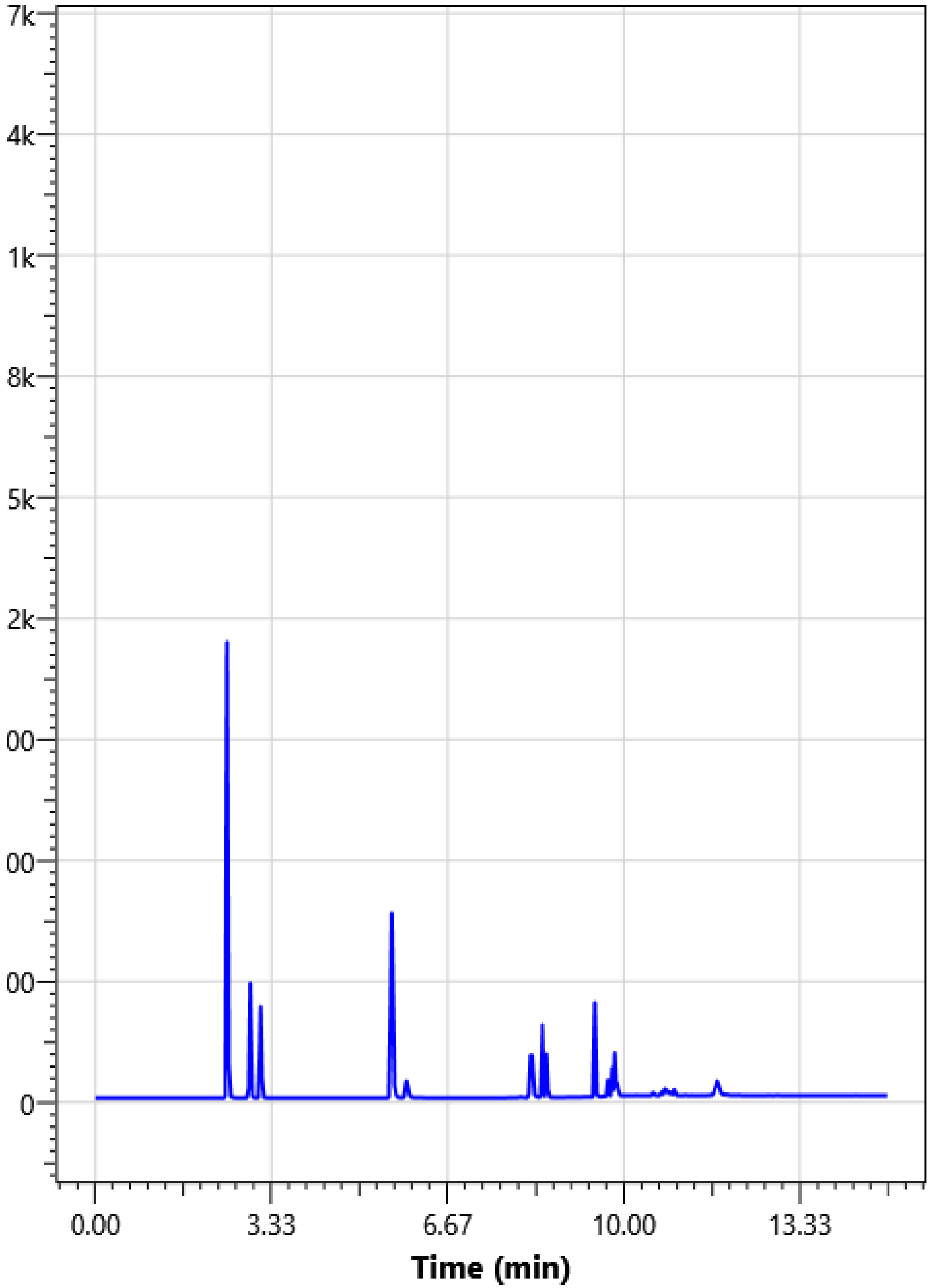
$$\mathrm{HHV} = 0.3491 \times \mathrm{C} + 1.1783 \times \mathrm{H} + 0.1034 \times \mathrm{O}$$

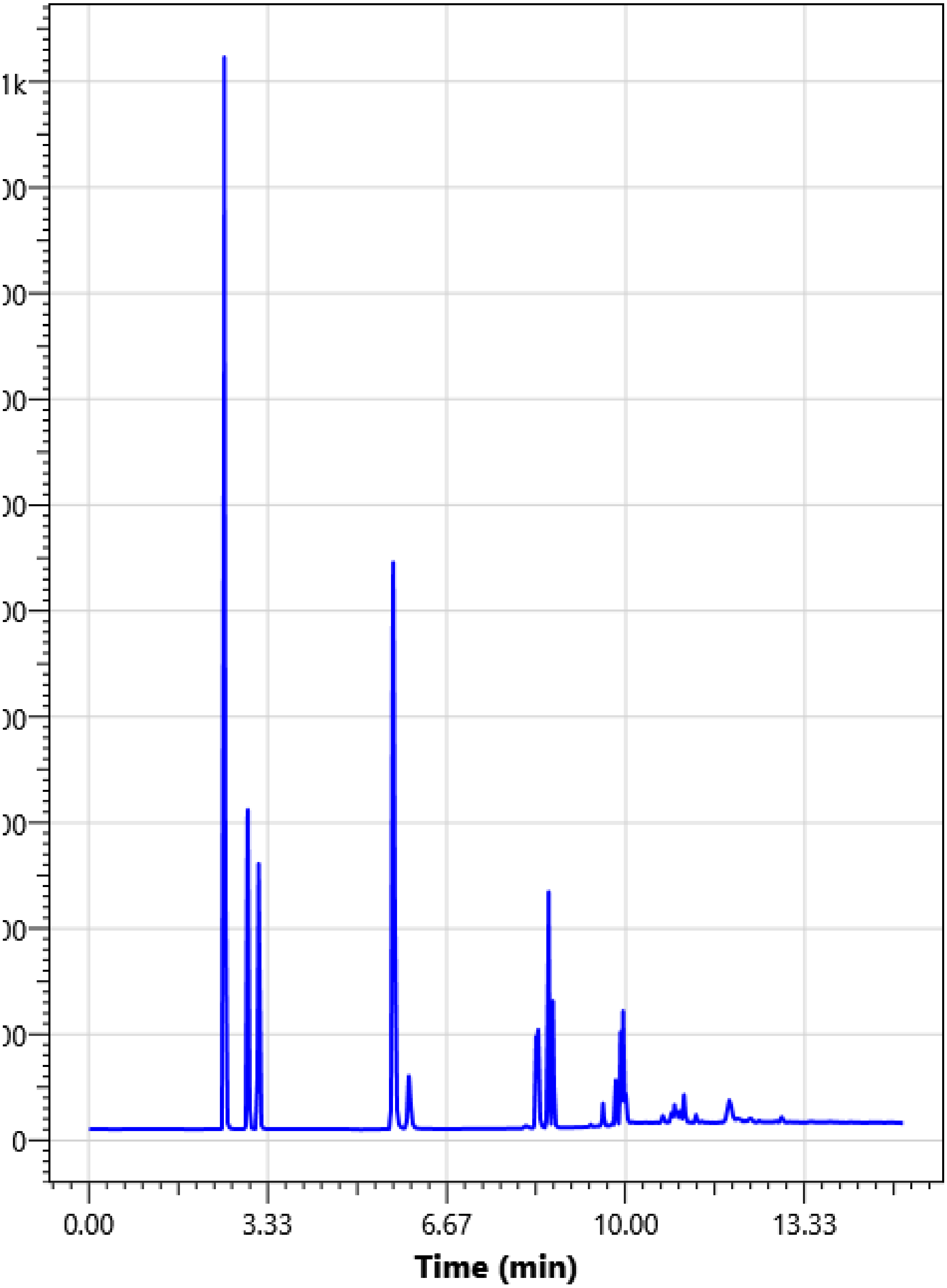
GC chromatograms:

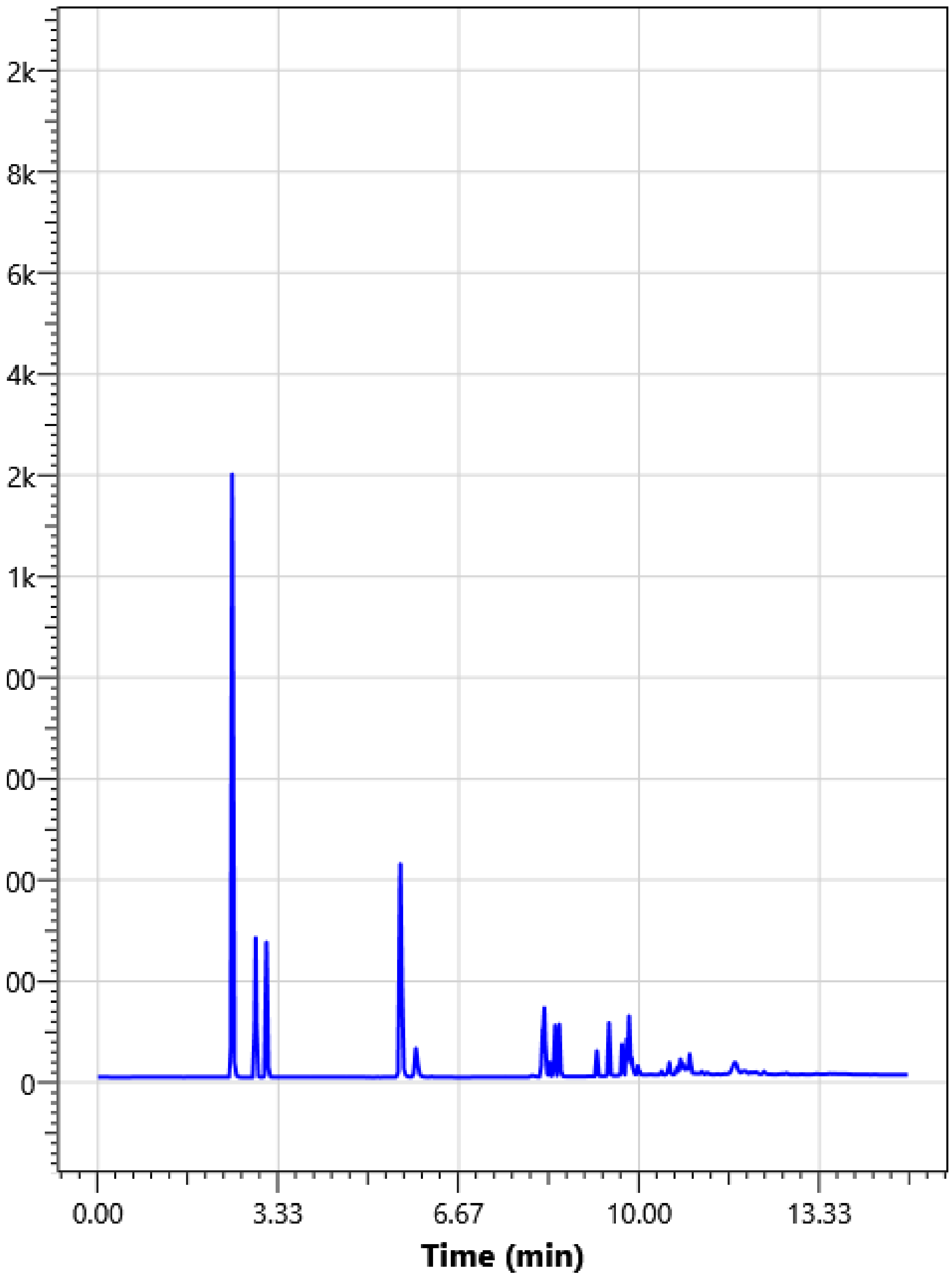
Gas sample chromatograms:

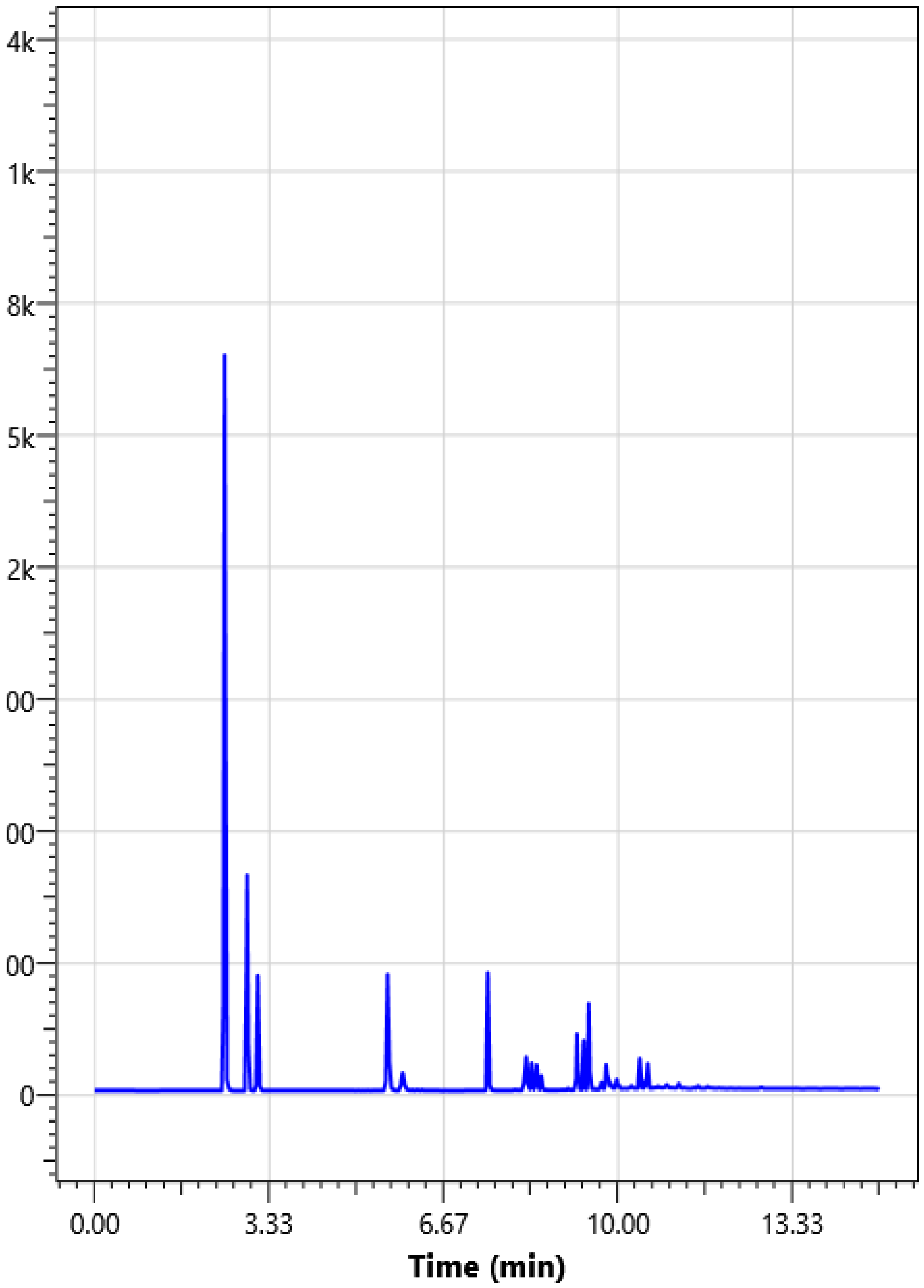


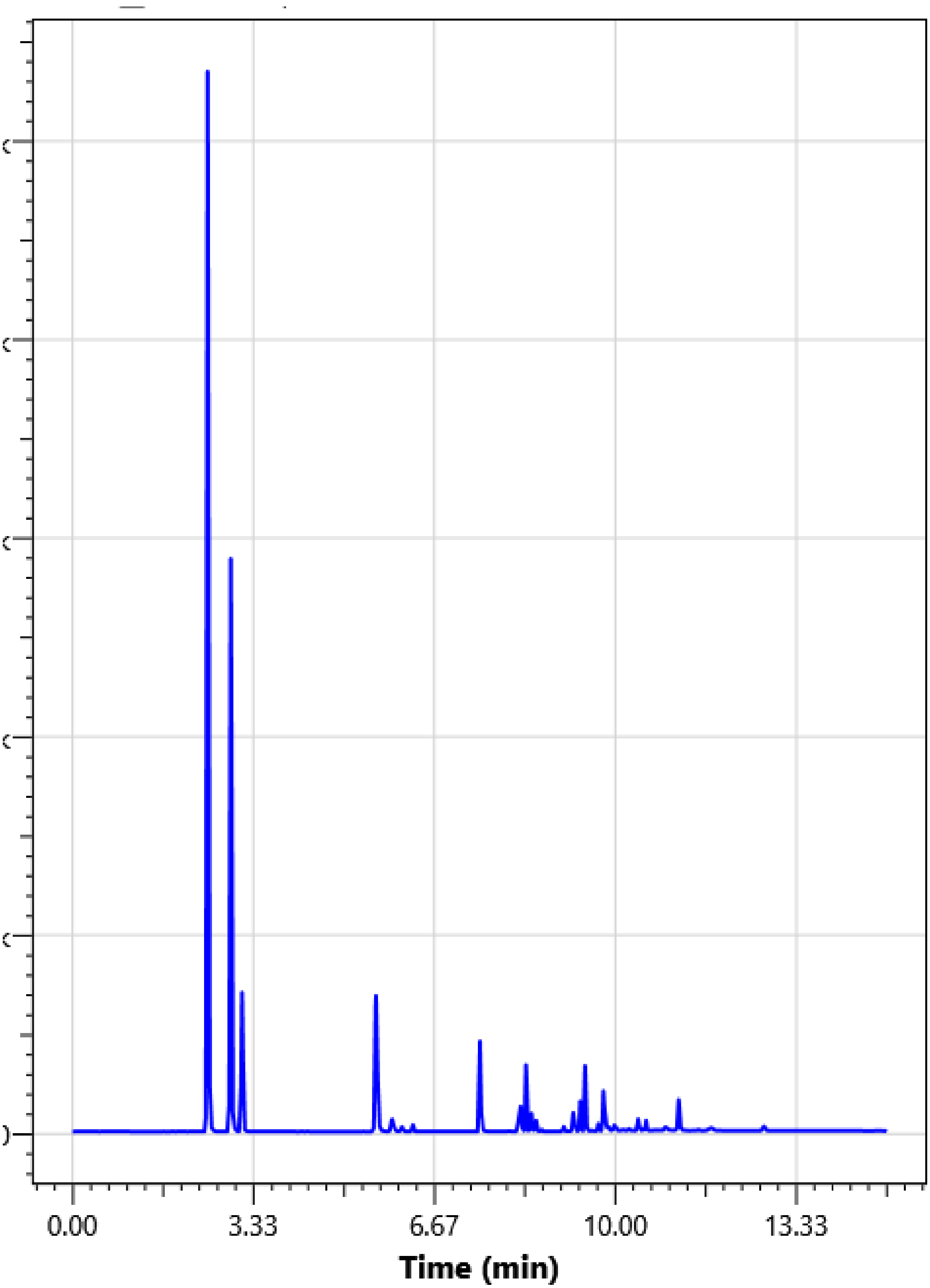

4k
1k
8k
5k
2k
00
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)

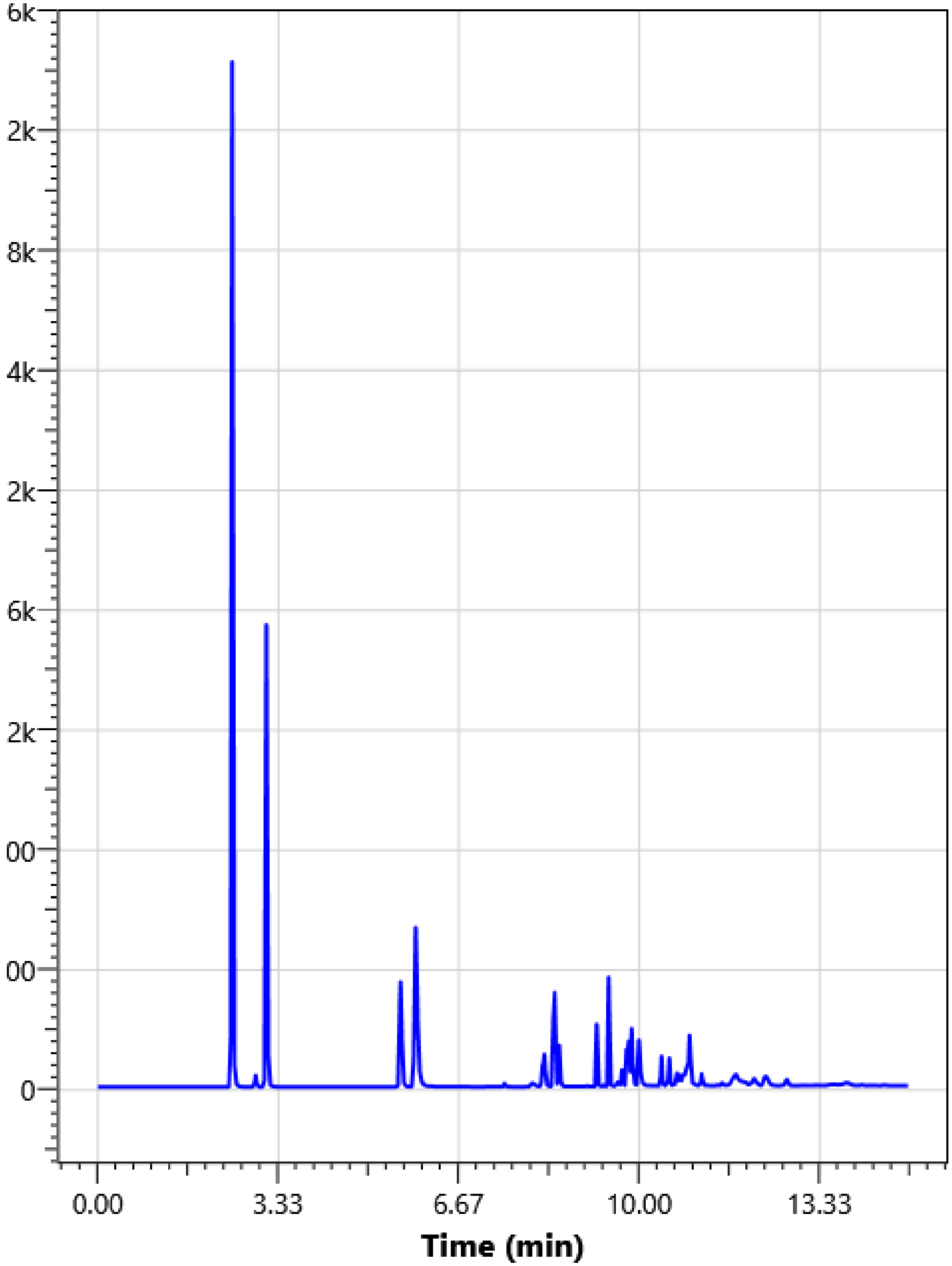

7k
4k
1k
8k
5k
2k
00
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)


1k
00
00
00
00
00
00
00
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)

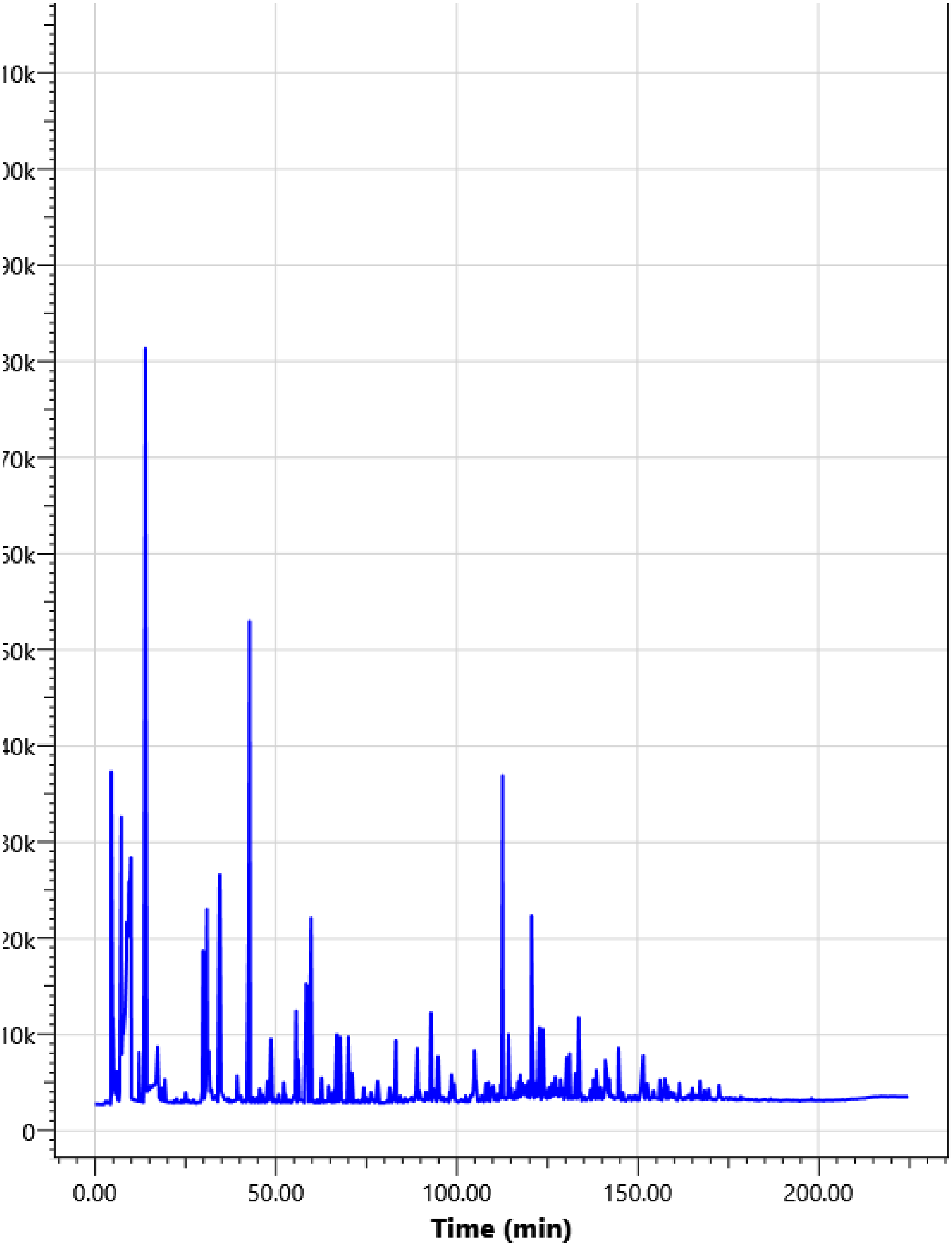

2k
8k
6k
4k
2k
1k
00
00
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)

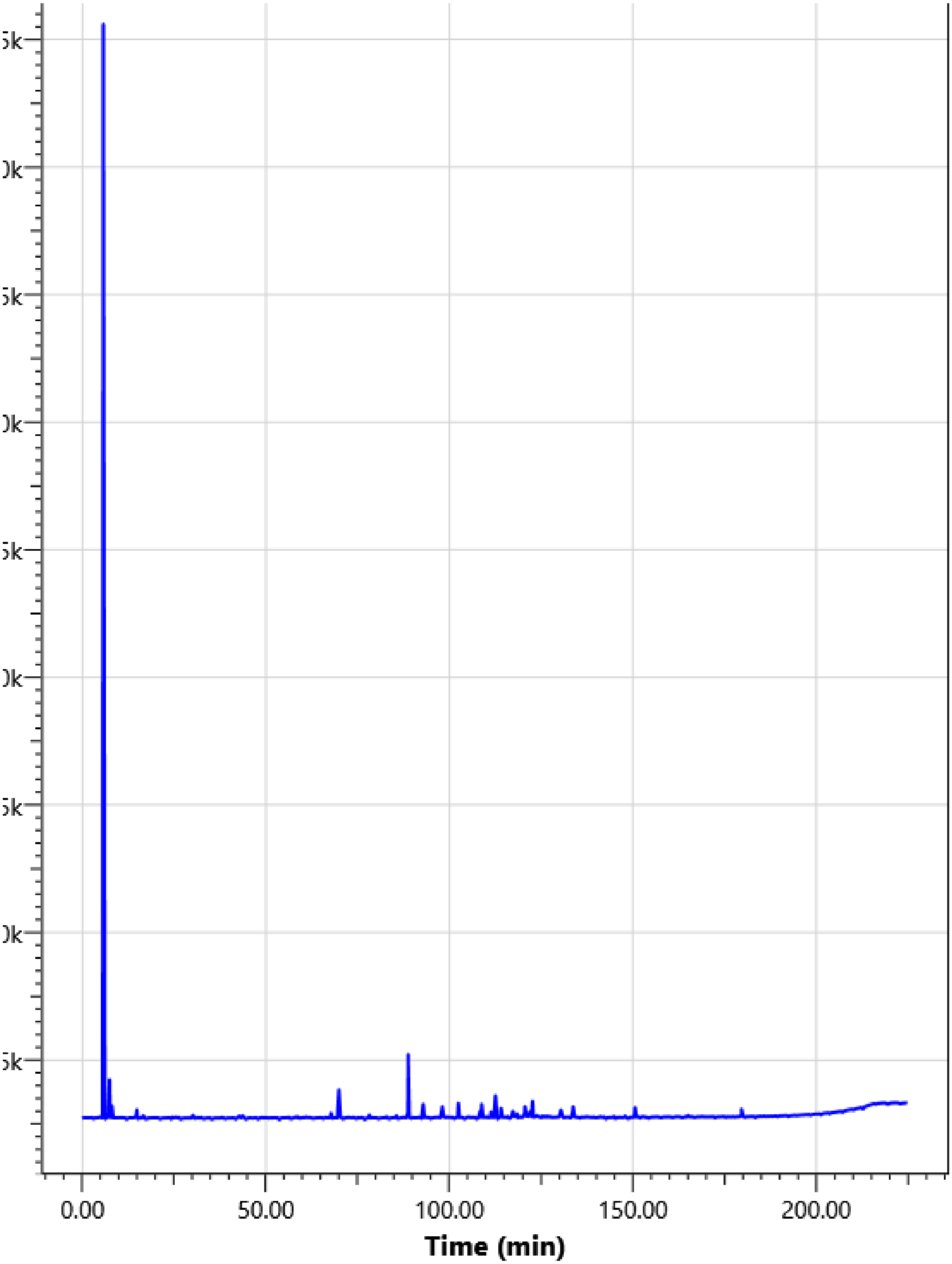

4k
1k
8k
5k
2k
00
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)

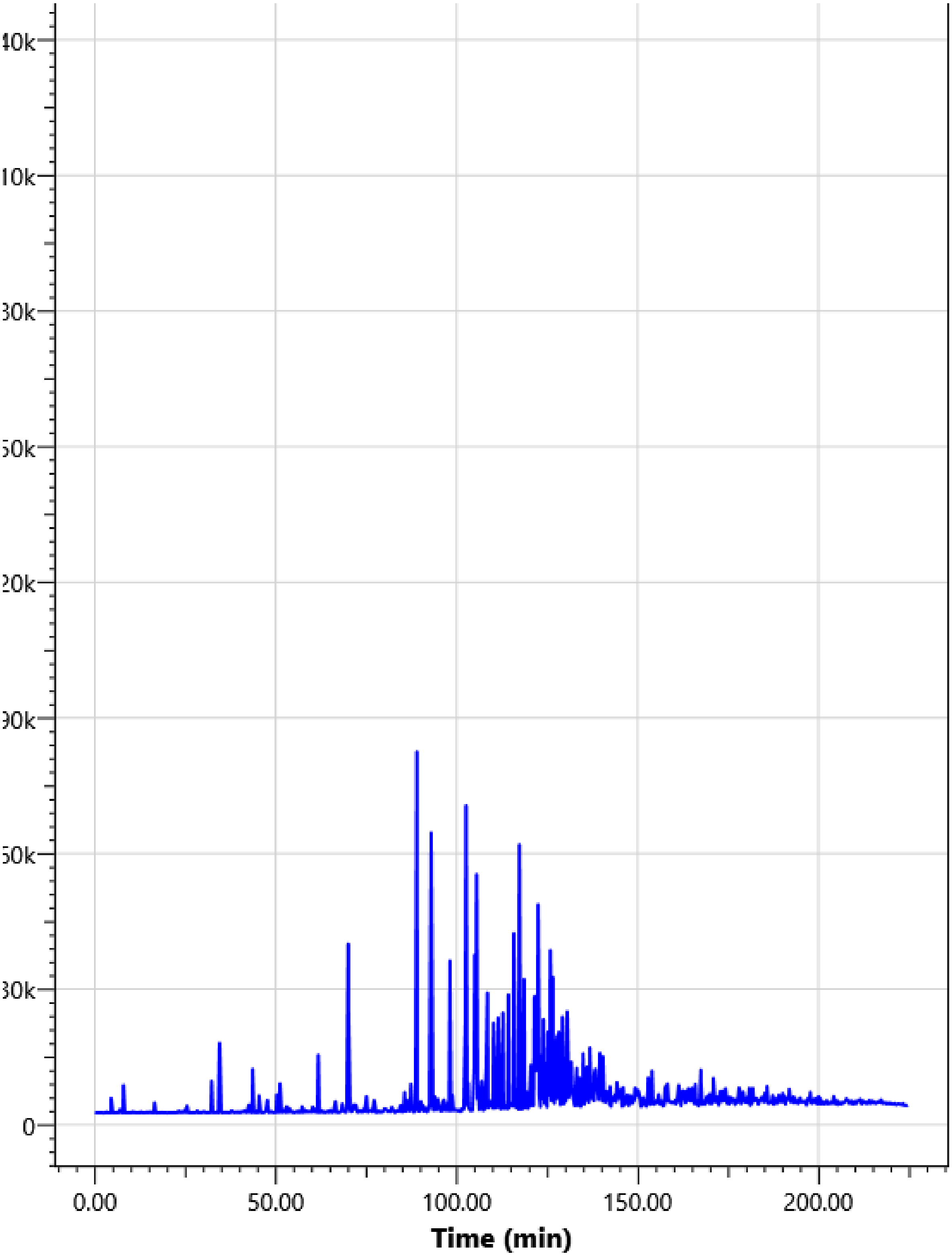

0.00
3.33
6.67
10.00
13.33
Time (min)

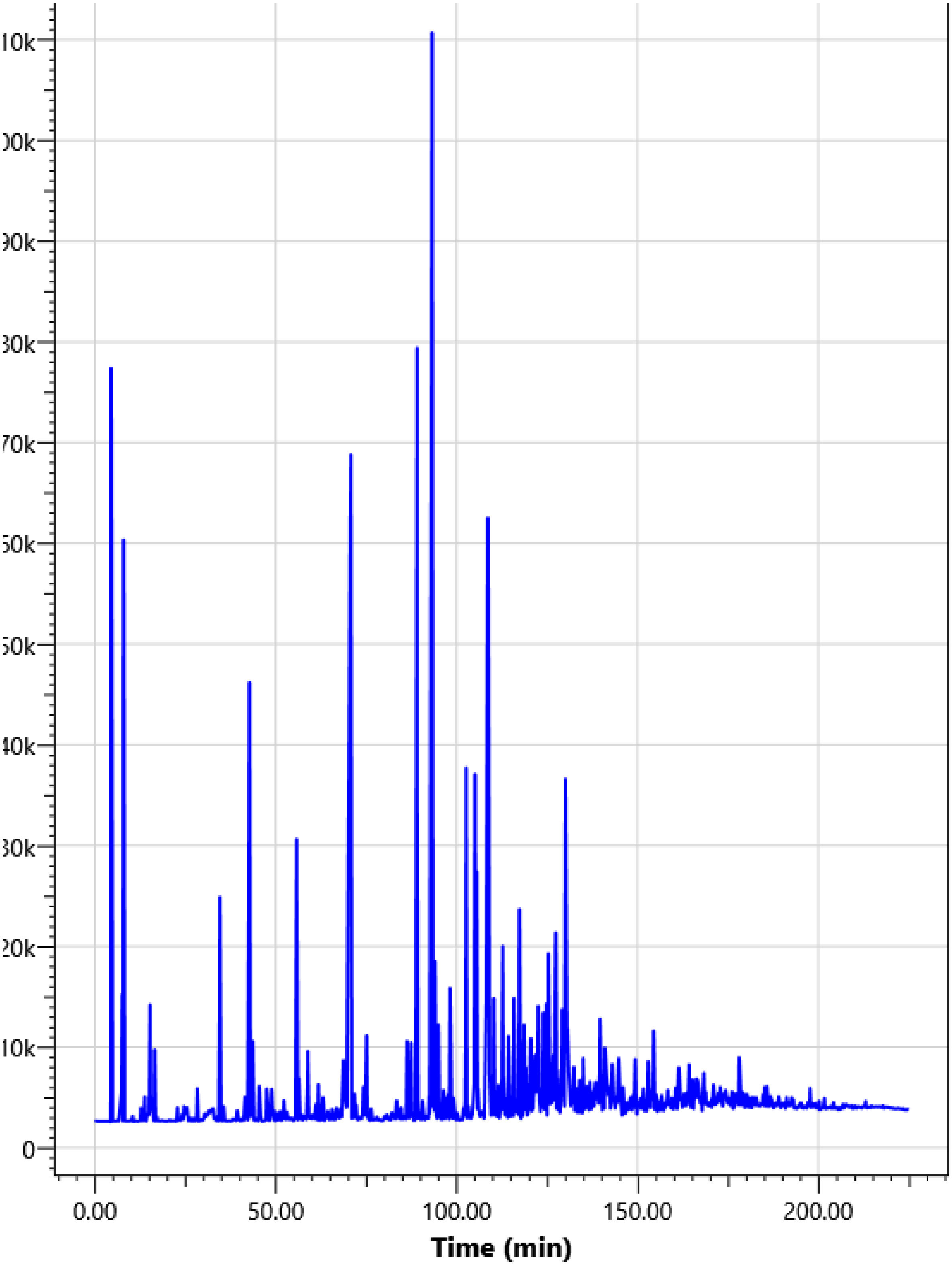

6k
2k
8k
4k
2k
6k
2k
00
00
0
0.00
3.33
6.67
10.00
13.33
Time (min)

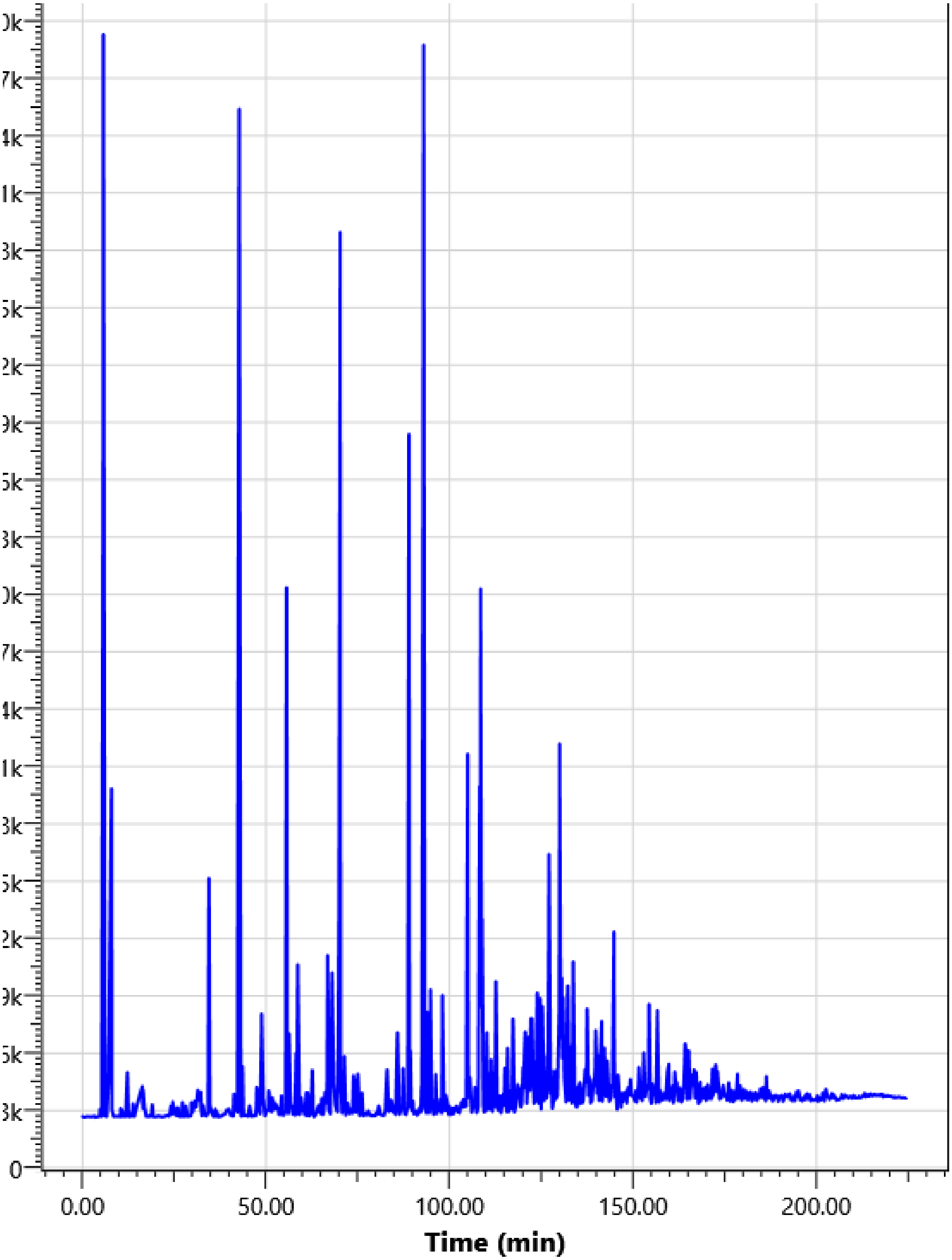
Liquid sample chromatograms:

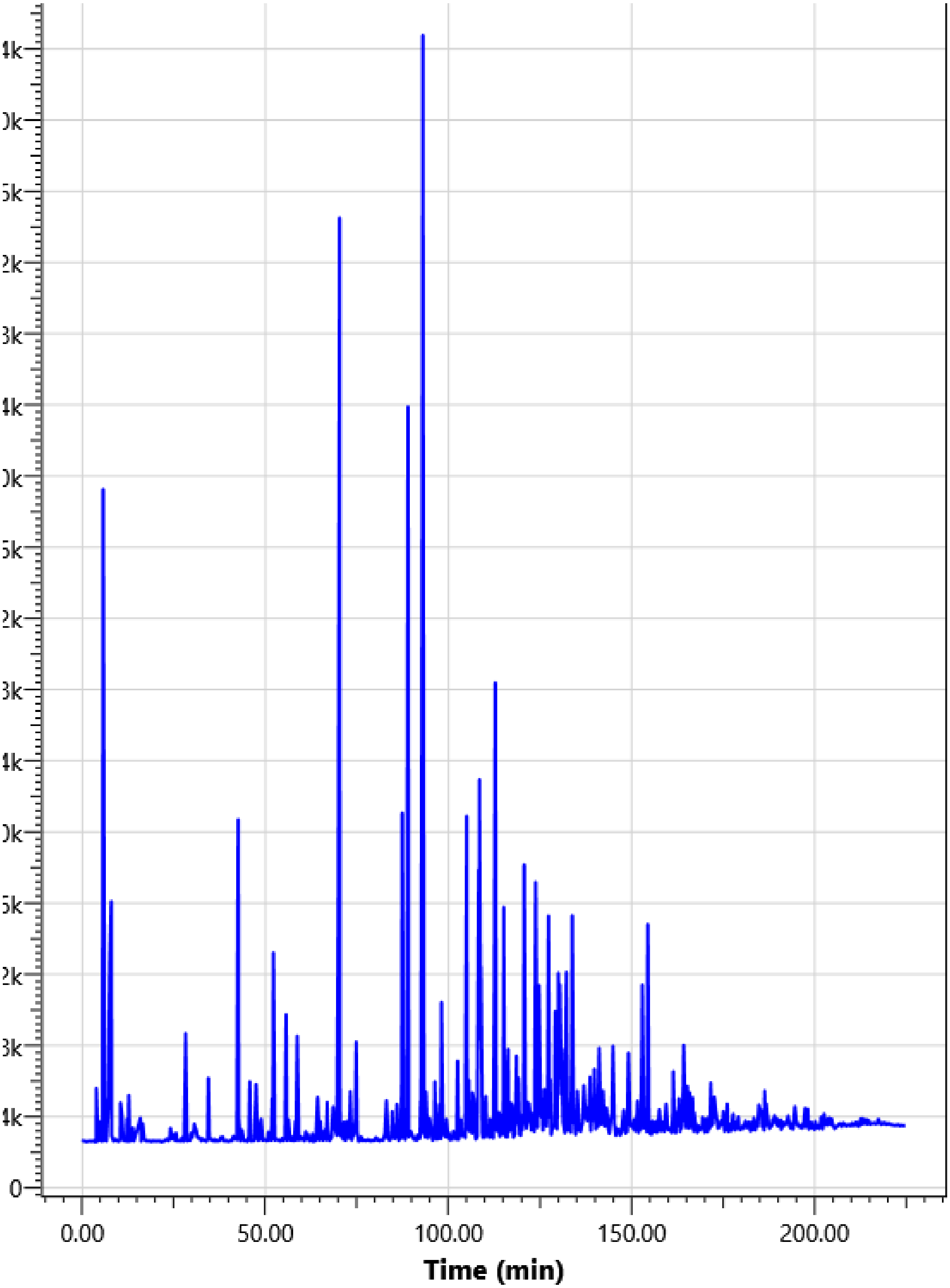


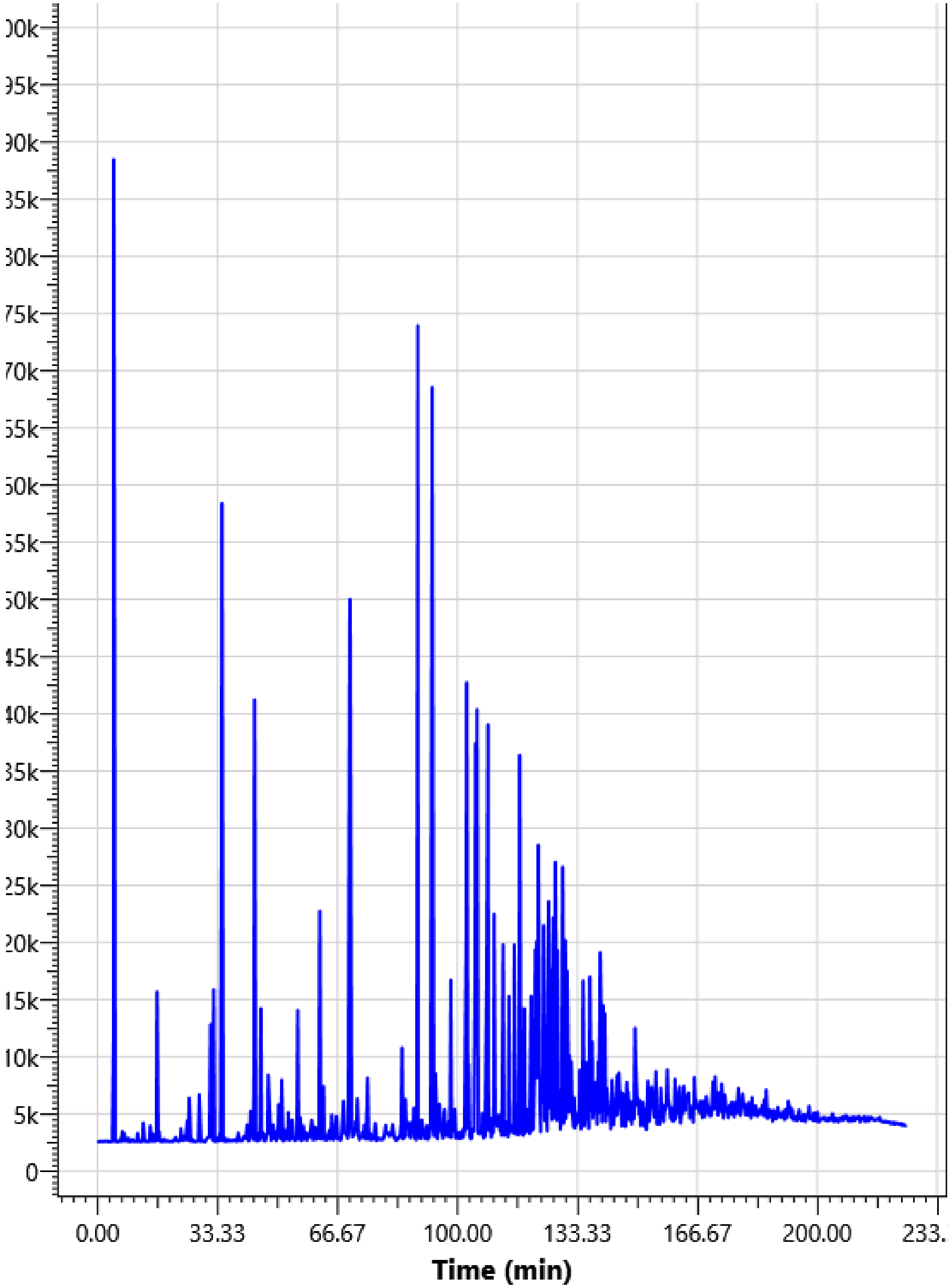

5k
0k
5k
0k
5k
0k
5k
0k
5k
0.00
50.00
100.00
150.00
200.00
Time (min)


40k
10k
30k
50k
20k
90k
50k
30k
0
0.00
50.00
100.00
150.00
200.00
Time (min)

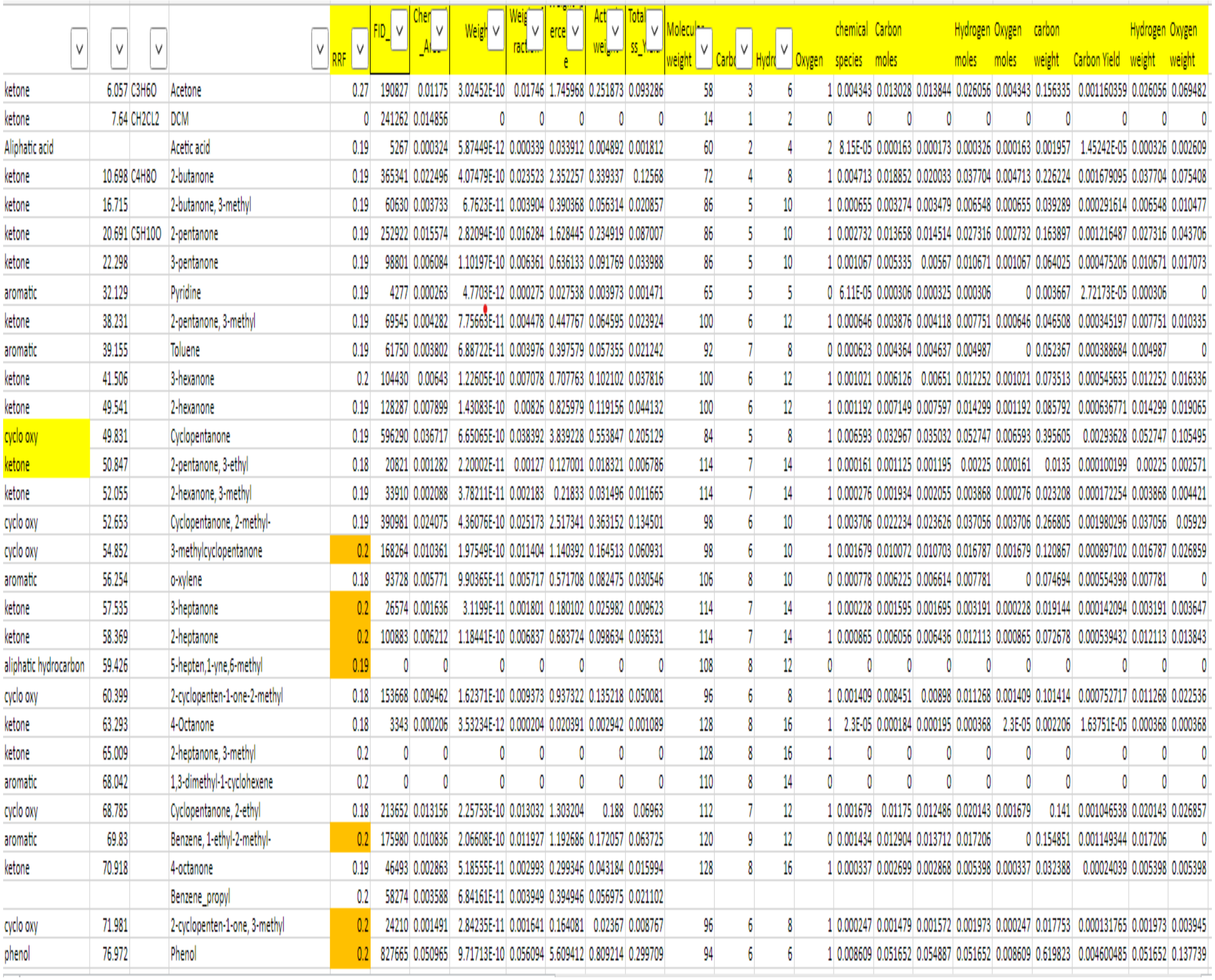

10k
00k
90k
30k
70k
50k
50k
40k
30k
20k
10k
0
0.00
50.00
100.00
150.00
200.00
Time (min)


0k
7k
4k
1k
8k
5k
2k
9k
6k
3k
0k
7k
4k
1k
8k
5k
2k
9k
6k
3k
0
0.00
50.00
100.00
150.00
200.00
Time (min)


4k
)k
5k
2k
3k
4k
)k
5k
2k
3k
4k
)k
5k
2k
3k
4k
0
0.00
50.00
100.00
150.00
200.00
Time (min)


0
5k
10k
15k
20k
25k
30k
35k
40k
45k
50k
55k
60k
65k
70k
75k
80k
85k
90k
95k
00k
0.00
33.33
66.67
100.00
133.33
166.67
200.00
233.
Time (min)

Data excel files:



				RRF	FID_	Cher _A	Weigh	Weig ract	erce e	Act wei	Total ss_Y	Molecul weight	Carb	Hydr	Oxygen	chemical species	Carbon moles		Hydrogen moles	Oxygen moles	carbon weight	Carbon Yield	Hydrogen weight	Oxygen weight
ketone	6.057	C3H6O	Acetone	0.27	190827	0.01175	3.02452E-10	0.01746	1.745968	0.251873	0.093286	58	3	6	1	0.004343	0.013028	0.013844	0.026056	0.004343	0.156335	0.001160359	0.026056	0.069482
ketone	7.64	CH2CL2	DCM	0	241262	0.014856	0	0	0	0	0	14	1	2	0	0	0	0	0	0	0	0	0	0
Aliphatic acid			Acetic acid	0.19	5267	0.000324	5.87449E-12	0.000339	0.033912	0.004892	0.001812	60	2	4	2	8.15E-05	0.000163	0.000173	0.000326	0.000163	0.001957	1.45242E-05	0.000326	0.002609
ketone	10.698	C4H8O	2-butanone	0.19	365341	0.022496	4.07479E-10	0.023523	2.352257	0.339337	0.12568	72	4	8	1	0.004713	0.018852	0.020033	0.037704	0.004713	0.226224	0.001679095	0.037704	0.075408
ketone	16.715		2-butanone, 3-methyl	0.19	60630	0.003733	6.7623E-11	0.003904	0.390368	0.056314	0.020857	86	5	10	1	0.000655	0.003274	0.003479	0.006548	0.000655	0.039289	0.000291614	0.006548	0.010477
ketone	20.691	C5H10O	2-pentanone	0.19	252922	0.015574	2.82094E-10	0.016284	1.628445	0.234919	0.087007	86	5	10	1	0.002732	0.013658	0.014514	0.027316	0.002732	0.163897	0.001216487	0.027316	0.043706
ketone	22.298		3-pentanone	0.19	98801	0.006084	1.10197E-10	0.006361	0.636133	0.091769	0.033988	86	5	10	1	0.001067	0.005335	0.00567	0.010671	0.001067	0.064025	0.000475206	0.010671	0.017073
aromatic	32.129		Pyridine	0.19	4277	0.000263	4.7703E-12	0.000275	0.027538	0.003973	0.001471	65	5	5	0	6.11E-05	0.000306	0.000325	0.000306	0	0.003667	2.72173E-05	0.000306	0
ketone	38.231		2-pentanone, 3-methyl	0.19	69545	0.004282	7.75663E-11	0.004478	0.447767	0.064595	0.023924	100	6	12	1	0.000646	0.003876	0.004118	0.007751	0.000646	0.046508	0.000345197	0.007751	0.010335
aromatic	39.155		Toluene	0.19	61750	0.003802	6.88722E-11	0.003976	0.397579	0.057355	0.021242	92	7	8	0	0.000623	0.004364	0.004637	0.004987	0	0.052367	0.000388684	0.004987	0
ketone	41.506		3-hexanone	0.2	104430	0.00643	1.22605E-10	0.007078	0.707763	0.102102	0.037816	100	6	12	1	0.001021	0.006126	0.00651	0.012252	0.001021	0.073513	0.000545635	0.012252	0.016336
ketone	49.541		2-hexanone	0.19	128287	0.007899	1.43083E-10	0.00826	0.825979	0.119156	0.044132	100	6	12	1	0.001192	0.007149	0.007597	0.014299	0.001192	0.085792	0.000636771	0.014299	0.019065
cyclo oxy	49.831		Cyclopentanone	0.19	596290	0.036717	6.65065E-10	0.038392	3.839228	0.553847	0.205129	84	5	8	1	0.006593	0.032967	0.035032	0.052747	0.006593	0.395605	0.00293628	0.052747	0.105495
ketone	50.847		2-pentanone, 3-ethyl	0.18	20821	0.001282	2.20002E-11	0.00127	0.127001	0.018321	0.006786	114	7	14	1	0.000161	0.001125	0.001195	0.00225	0.000161	0.0135	0.000100199	0.00225	0.002571
ketone	52.055		2-hexanone, 3-methyl	0.19	33910	0.002088	3.78211E-11	0.002183	0.21833	0.031496	0.011665	114	7	14	1	0.000276	0.001934	0.002055	0.003868	0.000276	0.023208	0.000172254	0.003868	0.004421
cyclo oxy	52.653		Cyclopentanone, 2-methyl-	0.19	390981	0.024075	4.36076E-10	0.025173	2.517341	0.363152	0.134501	98	6	10	1	0.003706	0.022234	0.023626	0.037056	0.003706	0.266805	0.001980296	0.037056	0.05929
cyclo oxy	54.852		3-methylcyclopentanone	0.2	168264	0.010361	1.97549E-10	0.011404	1.140392	0.164513	0.060931	98	6	10	1	0.001679	0.010072	0.010703	0.016787	0.001679	0.120867	0.000897102	0.016787	0.026859
aromatic	56.254		o-xylene	0.18	93728	0.005771	9.90365E-11	0.005717	0.571708	0.082475	0.030546	106	8	10	0	0.000778	0.006225	0.006614	0.007781	0	0.074694	0.000554398	0.007781	0
ketone	57.535		3-heptanone	0.2	26574	0.001636	3.1199E-11	0.001801	0.180102	0.025982	0.009623	114	7	14	1	0.000228	0.001595	0.001695	0.003191	0.000228	0.019144	0.000142094	0.003191	0.003647
ketone	58.369		2-heptanone	0.2	100883	0.006212	1.18441E-10	0.006837	0.683724	0.098634	0.036531	114	7	14	1	0.000865	0.006056	0.006436	0.012113	0.000865	0.072678	0.000539432	0.012113	0.013843
aliphatic hydrocarbon	59.426		5-hepten,1-yne,6-methyl	0.19	0	0	0	0	0	0	0	108	8	12	0	0	0	0	0	0	0	0	0	0
cyclo oxy	60.399		2-cyclopenten-1-one-2-methyl	0.18	153668	0.009462	1.62371E-10	0.009373	0.937322	0.135218	0.050081	96	6	8	1	0.001409	0.008451	0.00898	0.011268	0.001409	0.101414	0.000752717	0.011268	0.022536
ketone	63.293		4-Octanone	0.18	3343	0.000206	3.53234E-12	0.000204	0.020391	0.002942	0.001089	128	8	16	1	2.3E-05	0.000184	0.000195	0.000368	2.3E-05	0.002206	1.63751E-05	0.000368	0.000368
ketone	65.009		2-heptanone, 3-methyl	0.2	0	0	0	0	0	0	0	128	8	16	1	0	0	0	0	0	0	0	0	0
aromatic	68.042		1,3-dimethyl-1-cyclohexene	0.2	0	0	0	0	0	0	0	110	8	14	0	0	0	0	0	0	0	0	0	0
cyclo oxy	68.785		Cyclopentanone, 2-ethyl	0.18	213652	0.013156	2.25753E-10	0.013032	1.303204	0.188	0.06963	112	7	12	1	0.001679	0.01175	0.012486	0.020143	0.001679	0.141	0.001046538	0.020143	0.026857
aromatic	69.83		Benzene, 1-ethyl-2-methyl-	0.2	175980	0.010836	2.06608E-10	0.011927	1.192686	0.172057	0.063725	120	9	12	0	0.001434	0.012904	0.013712	0.017206	0	0.154851	0.001149344	0.017206	0
ketone	70.918		4-octanone	0.19	46493	0.002863	5.18555E-11	0.002993	0.299346	0.043184	0.015994	128	8	16	1	0.000337	0.002699	0.002868	0.005398	0.000337	0.032388	0.00024039	0.005398	0.005398
			Benzene_propyl	0.2	58274	0.003588	6.84161E-11	0.003949	0.394946	0.056975	0.021102													
cyclo oxy	71.981		2-cyclopenten-1-one, 3-methyl	0.2	24210	0.001491	2.84235E-11	0.001641	0.164081	0.02367	0.008767	96	6	8	1	0.000247	0.001479	0.001572	0.001973	0.000247	0.017753	0.000131765	0.001973	0.003945
phenol	76.972		Phenol	0.2	827665	0.050965	9.71713E-10	0.056094	5.609412	0.809214	0.299709	94	6	6	1	0.008609	0.051652	0.054887	0.051652	0.008609	0.619823	0.004600485	0.051652	0.137739

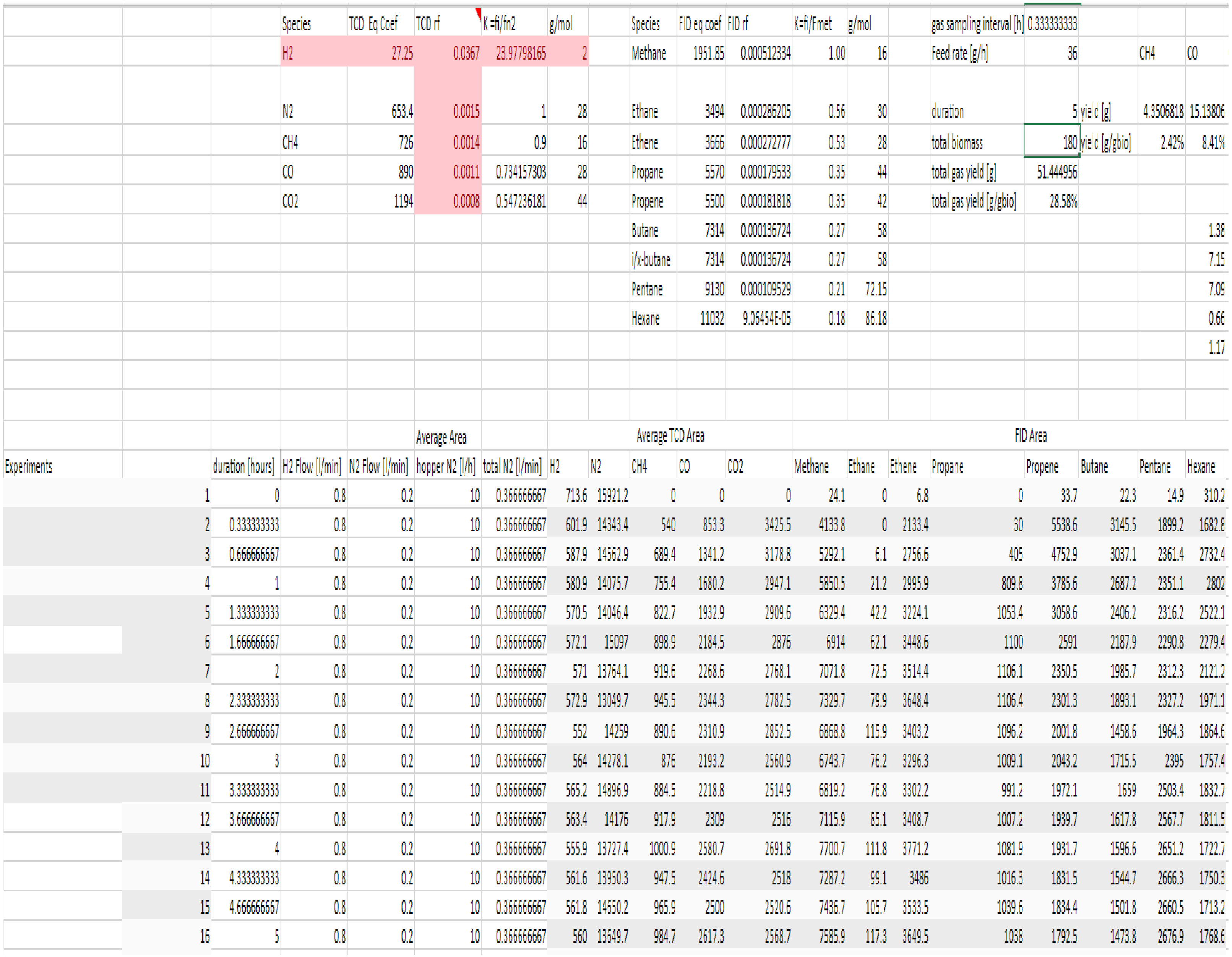
ketone	79.389		2-Octanone	0.18	18862	0.001161	1.99303E-11	0.001151	0.115052	0.016597	0.006147	128	8	16	1	0.00013	0.001037	0.001102	0.002075	0.00013	0.012448	9.23923E-05	0.002075	0.002075
cyclo oxy	81.461		Cyclopentanone, 2-methyl	0.17	59793	0.003682	5.96695E-11	0.003445	0.344455	0.049691	0.018404	126	8	14	1	0.000394	0.003155	0.003353	0.005521	0.000394	0.03786	0.000281005	0.005521	0.00631
aromatic	81.878		Benzene, 1,2,3-trimethyl	0.2	97473	0.006002	1.14437E-10	0.006606	0.660613	0.0953	0.035296	120	9	12	0	0.000794	0.007148	0.007595	0.00953	0	0.08577	0.000636607	0.00953	0
cyclo oxy	82.603		2-cyclopenten-1-one, 2,3-dimethyl	0.2	27817	0.001713	3.26583E-11	0.001885	0.188527	0.027197	0.010073	110	7	10	1	0.000247	0.001731	0.001839	0.002472	0.000247	0.020769	0.000154149	0.002472	0.003956
aliphatic hydrocarbon	83.304		2,3-dimethyl-3-heptene,	0.19	0	0	0	0	0	0	0	126	9	18	0	0	0	0	0	0	0	0	0	0
aromatic	85.89		Mestylene	0.2	25450	0.001567	2.98793E-11	0.001725	0.172485	0.024883	0.009216	120	9	12	0	0.000207	0.001866	0.001983	0.002488	0	0.022394	0.000166217	0.002488	0
aromatic	86.627		1-Isopropylcyclohex-1-ene	0.17	28680	0.001766	2.86208E-11	0.001652	0.165219	0.023835	0.008828	124	9	16	0	0.000192	0.00173	0.001838	0.003075	0	0.020759	0.000154079	0.003075	0
aromatic	88.337		Indane	0.2	115479	0.007111	1.35577E-10	0.007826	0.782647	0.112905	0.041817	118	9	10	0	0.000957	0.008611	0.009151	0.009568	0	0.103336	0.000766989	0.009568	0
cyclo oxy	91.449		2-n-Hexylcyclopentanone	0.17	68679	0.004229	6.85372E-11	0.003956	0.395645	0.057076	0.021139	168	11	20	1	0.00034	0.003737	0.003971	0.006795	0.00034	0.044845	0.000332853	0.006795	0.005436
cyclo oxy	93.038		2-cyclopenten-1-one, 2,3-dimethyl'	0.2	0	0	0	0	0	0	0	110	7	10	1	0	0	0	0	0	0	0	0	0
aromatic	94.004		Indene	0.2	28499	0.001755	3.3459E-11	0.001931	0.193149	0.027864	0.01032	116	9	8	0	0.00024	0.002162	0.002297	0.001922	0	0.025942	0.000192548	0.001922	0
			Benzene,1-2 diethyl	0.2	56855	0.003501	6.67501E-11	0.003853	0.385329	0.055588	0.020588													
phenol	94.427		Phenol,2-methyl	0.17	850142	0.052349	8.48386E-10	0.048975	4.897486	0.706511	0.261671	108	7	8	1	0.006542	0.045792	0.04866	0.052334	0.006542	0.549509	0.004078593	0.052334	0.104668
cyclo oxy	95.46		2-cyclopenten-1-one,3,4,4-trimethyl	0.17	21131	0.001301	2.10874E-11	0.001217	0.121731	0.017561	0.006504	124	8	12	1	0.000142	0.001133	0.001204	0.001699	0.000142	0.013596	0.00010091	0.001699	0.002266
ketone	95.781		4-Nonanone	0.12	0	0	0	0	0	0	0	142	9	18	1	0	0	0	0	0	0	0	0	0
phenol	96.536		2,3-Dimethylhydroquinone	0.16	21131	0.001301	1.98469E-11	0.001146	0.114571	0.016528	0.006121	138	8	10	2	0.00012	0.000958	0.001018	0.001198	0.00024	0.011498	8.53388E-05	0.001198	0.003833
aromatic	97.63		cymene	0.17	15084	0.000929	1.50528E-11	0.000869	0.086896	0.012536	0.004643	134	10	14	0	9.35E-05	0.000935	0.000994	0.00131	0	0.011226	8.33213E-05	0.00131	0
phenol	97.962		Phenol,3-methyl	0.2	955313	0.058825	1.12158E-09	0.064745	6.474533	0.934016	0.345932	108	7	8	1	0.008648	0.060538	0.06433	0.069186	0.008648	0.726457	0.005391947	0.069186	0.138373
aromatic	100.433		1H-Indene,2,3-dihydro-4-methyl-	0.16	53189	0.003275	4.99569E-11	0.002884	0.288386	0.041603	0.015408	132	10	12	0	0.000315	0.003152	0.003349	0.003782	0	0.037821	0.000280714	0.003782	0
furan	96.33		2(3H)-Benzofuran	0.16	61110	0.003763	5.73965E-11	0.003313	0.331333	0.047798	0.017703	152	9	12	2	0.000314	0.00283	0.003007	0.003774	0.000629	0.033962	0.000252073	0.003774	0.010063
aromatic	101.533		2-Carene	0.2	49262	0.003033	5.78356E-11	0.003339	0.333868	0.048164	0.017838	136	10	16	0	0.000354	0.003541	0.003763	0.005666	0	0.042497	0.000315427	0.005666	0
phenol	102.977		Phenol,2,6-dimethyl-	0.2	263530	0.016227	3.09395E-10	0.01786	1.786047	0.257655	0.095428	122	8	10	1	0.002112	0.016895	0.017954	0.021119	0.002112	0.202745	0.001504825	0.021119	0.033791
furan	105.206		Benzofuran,2-methyl	0.2	16746	0.001031	1.96605E-11	0.001135	0.113494	0.016373	0.006064	132	9	8	1	0.000124	0.001116	0.001186	0.000992	0.000124	0.013396	9.94272E-05	0.000992	0.001985
cyclo oxy	107.212		3-cyclopenten-1-one,2,2,5,5-tetramethyl	0.15	21763	0.00134	1.9163E-11	0.001106	0.110622	0.015958	0.005911	138	9	14	1	0.000116	0.001041	0.001106	0.001619	0.000116	0.012489	9.26977E-05	0.001619	0.00185
phenol	107.544		Phenol,2-ethyl-	0.18	431219	0.026553	4.55642E-10	0.026303	2.630287	0.379445	0.140535	122	8	10	1	0.00311	0.024882	0.02644	0.031102	0.00311	0.29858	0.002216135	0.031102	0.049763
aromatic	108.372		1H-Indene,2,3-dihydro-4-methyl-'	0.2	87164	0.005367	1.02334E-10	0.005907	0.590745	0.085221	0.031563	132	10	12	0	0.000646	0.006456	0.00686	0.007747	0	0.077473	0.000575028	0.007747	0
phenol	110.964		Phenol, 2,4-dimethyl	0.2	445416	0.027427	5.22937E-10	0.030188	3.01876	0.435486	0.161291	122	8	10	1	0.00357	0.028556	0.030345	0.035696	0.00357	0.342678	0.002543441	0.035696	0.057113
phenol	111.399		Phenol, 2,5-dimethyl	0.16	395892	0.024378	3.71835E-10	0.021465	2.146493	0.309653	0.114686	122	8	10	1	0.002538	0.020305	0.021577	0.025381	0.002538	0.243661	0.001808517	0.025381	0.04061
aromatic	111.973		2-methylindene	0.2	0	0	0	0	0	0	0	130	10	10	0	0	0	0	0	0	0	0	0	0
aromatic	112.293		2-methylindene'	0.13	25763	0.001586	1.96604E-11	0.001135	0.113494	0.016373	0.006064	130	10	10	0	0.000126	0.001259	0.001338	0.001259	0	0.015113	0.000112174	0.001259	0
phenol	113.756		Phenol, 3-ethyl-	0.2	532893	0.032814	6.25638E-10	0.036116	3.611626	0.521013	0.192968	122	8	10	1	0.004271	0.034165	0.036305	0.042706	0.004271	0.409978	0.003042957	0.042706	0.06833
phenol	114.178		Phenol, 3,5-dimethyl	0.12	158826	0.00978	1.11881E-10	0.006459	0.645856	0.093171	0.034508	122	8	10	1	0.000764	0.00611	0.006492	0.007637	0.000764	0.073315	0.000544163	0.007637	0.012219
phenol	115.036		Phenol, 2,3-dimethyl	0.12	175294	0.010794	1.23481E-10	0.007128	0.712822	0.102832	0.038086	122	8	10	1	0.000843	0.006743	0.007165	0.008429	0.000843	0.080917	0.000600584	0.008429	0.013486

phenol	115.254		Phenol, 2-ethyl-4-methyl	0.12	190949	0.011758	1.34509E-10	0.007765	0.776482	0.112015	0.041487	136	9	12	1	0.000824	0.007413	0.007877	0.009884	0.000824	0.088953	0.000660234	0.009884	0.013178
phenol	116.058		Phenol, 3,4-dimethyl	0.18	221397	0.013633	2.33936E-10	0.013504	1.350445	0.194815	0.072154	122	8	10	1	0.001597	0.012775	0.013575	0.015968	0.001597	0.153297	0.001137811	0.015968	0.02555
phenol	116.414		Phenol, 2,3,5-trimethyl-	0.15	152466	0.009388	1.34251E-10	0.00775	0.774992	0.1118	0.041408	136	9	12	1	0.000822	0.007399	0.007862	0.009865	0.000822	0.088783	0.000658967	0.009865	0.013153
phenol	117.042		Phenol, 2-propyl	0.16	149435	0.009202	1.40354E-10	0.008102	0.810224	0.116883	0.04329	136	9	12	1	0.000859	0.007735	0.008219	0.010313	0.000859	0.092819	0.000688924	0.010313	0.013751
phenol	117.556		Phenol, 2-ethyl-4-methyl'	0.2	227536	0.014011	2.67137E-10	0.015421	1.542101	0.222464	0.082394	136	9	12	1	0.001636	0.014722	0.015644	0.019629	0.001636	0.176662	0.001311231	0.019629	0.026172
phenol	118.637		Phenol, 2-ethyl-5-methyl	0.16	261730	0.016116	2.45825E-10	0.014191	1.419078	0.204716	0.075821	136	9	12	1	0.001505	0.013547	0.014396	0.018063	0.001505	0.162569	0.001206626	0.018063	0.024084
phenol	119.628		Phenol, 2-ethyl-4-methyl''	0.15	450953	0.027768	3.97078E-10	0.022922	2.292215	0.330675	0.122472	136	9	12	1	0.002431	0.021883	0.023253	0.029177	0.002431	0.262595	0.001949045	0.029177	0.038903
phenol	120.245		Phenol, 2-ethyl-4-methyl'''	0.12	187586	0.011551	1.3214E-10	0.007628	0.762807	0.110042	0.040756	136	9	12	1	0.000809	0.007282	0.007738	0.00971	0.000809	0.087387	0.000648606	0.00971	0.012946
phenol	121.139		2,5-Diethylphenol	0.2	688372	0.042387	8.08177E-10	0.046654	4.665369	0.673026	0.249269	150	10	14	1	0.004487	0.044868	0.047679	0.062816	0.004487	0.538421	0.003996295	0.062816	0.071789
phenol	122.281		Phenol, 2,3,5-trimethyl-'	0.16	162198	0.009988	1.52342E-10	0.008794	0.879424	0.126866	0.046987	136	9	12	1	0.000933	0.008396	0.008921	0.011194	0.000933	0.100746	0.000747764	0.011194	0.014925
phenol	122.595		Phenol, 2,3,5-trimethyl-''	0.19	112119	0.006904	1.25051E-10	0.007219	0.721881	0.104139	0.03857	136	9	12	1	0.000766	0.006892	0.007323	0.009189	0.000766	0.082698	0.000613807	0.009189	0.012252
phenol	122.964		phenol, 2,3,5,6-tetramethyl-	0.19	195262	0.012024	2.17783E-10	0.012572	1.257199	0.181364	0.067172	150	10	14	1	0.001209	0.012091	0.012848	0.016927	0.001209	0.145091	0.001076901	0.016927	0.019345
phenol	123.628		Thymol	0.19	3	1.85E-07	3.34602E-15	1.93E-07	1.93E-05	2.79E-06	1.03E-06	150	10	14	1	1.86E-08	1.86E-07	1.97E-07	2.6E-07	1.86E-08	2.23E-06	1.65455E-08	2.6E-07	2.97E-07
phenol	124.22		Thymol'	0.19	222180	0.013681	2.47806E-10	0.014305	1.430511	0.206366	0.076432	150	10	14	1	0.001376	0.013758	0.014619	0.019261	0.001376	0.165092	0.001225358	0.019261	0.022012
phenol	124.45		Phenol, 3,5-diethyl	0.19	205034	0.012625	2.28682E-10	0.013201	1.320117	0.19044	0.070533	150	10	14	1	0.00127	0.012696	0.013491	0.017774	0.00127	0.152352	0.001130795	0.017774	0.020314
phenol	124.788		Phenol, 3,5-diethyl'	0.19	102010	0.006281	1.13776E-10	0.006568	0.656794	0.094749	0.035092	150	10	14	1	0.000632	0.006317	0.006712	0.008843	0.000632	0.075799	0.000562601	0.008843	0.010107
aromatic	125.797		1H-Indene, 1-ethylindene-	0.19	112470	0.006925	1.25442E-10	0.007241	0.724141	0.104465	0.038691	150	10	14	1	0.000696	0.006964	0.0074	0.00975	0.000696	0.083572	0.00062029	0.00975	0.011143
phenol	126.444		Thymol''	0.19	202677	0.01248	2.26054E-10	0.013049	1.304941	0.188251	0.069723	150	10	14	1	0.001255	0.01255	0.013336	0.01757	0.001255	0.150601	0.001117796	0.01757	0.02008
phenol	127.67		Benzene, 1-methoxy-4-propyl-	0.19	408780	0.025171	4.55928E-10	0.026319	2.63194	0.379684	0.140624	150	10	14	1	0.002531	0.025312	0.026898	0.035437	0.002531	0.303747	0.002254486	0.035437	0.0405
phenol	127.845		Phenol, 2-(1-methylpropyl)-	0.19	92369	0.005688	1.03023E-10	0.005947	0.59472	0.085794	0.031776	164	11	16	1	0.000523	0.005754	0.006115	0.00837	0.000523	0.069054	0.000512536	0.00837	0.00837
phenol	128.293		Benzene, 1-methoxy-4-(1-methylpropyl)-	0.19	22550	0.001389	2.51509E-11	0.001452	0.145189	0.020945	0.007757	164	11	16	1	0.000128	0.001405	0.001493	0.002043	0.000128	0.016858	0.000125125	0.002043	0.002043
phenol	128.734		Benzene, 1-methoxy-4-methyl-2-1(1-methy	0.19	289969	0.017855	3.23414E-10	0.01867	1.866973	0.269329	0.099752	164	11	16	1	0.001642	0.018065	0.019196	0.026276	0.001642	0.216777	0.001608976	0.026276	0.026276
phenol	129.894		Benzene, 1-methoxy-4-methyl-2-1(1-methy	0.19	79540	0.004898	8.87141E-11	0.005121	0.51212	0.073878	0.027362	164	11	16	1	0.00045	0.004955	0.005266	0.007208	0.00045	0.059463	0.000441351	0.007208	0.007208
phenol	130.534		Benzene, 1-methoxy-4-(1-methylpropyl)-'	0.19	14234	0.000876	1.58757E-11	0.000916	0.091646	0.013221	0.004897	164	11	16	1	8.06E-05	0.000887	0.000942	0.00129	8.06E-05	0.010641	7.89814E-05	0.00129	0.00129
phenol	132.129		2-ethyl-5-n-propylphenol-	0.19	168173	0.010355	1.8757E-10	0.010828	1.082786	0.156203	0.057853	164	11	16	1	0.000952	0.010477	0.011133	0.015239	0.000952	0.125724	0.000933156	0.015239	0.015239
phenol	133.048		2-ethyl-5-n-propylphenol-'	0.19	145316	0.008948	1.62077E-10	0.009356	0.935621	0.134973	0.04999	164	11	16	1	0.000823	0.009053	0.00962	0.013168	0.000823	0.108637	0.000806328	0.013168	0.013168
phenol	133.845		Propofol	0.19	18561	0.001143	2.07018E-11	0.001195	0.119505	0.01724	0.006385	178	12	18	1	9.69E-05	0.001162	0.001235	0.001743	9.69E-05	0.013947	0.000103517	0.001743	0.00155
aromatic	134.552		Napthalene	0.19	222905	0.013726	2.48615E-10	0.014352	1.435179	0.207039	0.076681	156	12	12	0	0.001327	0.015926	0.016924	0.015926	0	0.191113	0.001418488	0.015926	0
aromatic	135.06		1,3-cyclopentadiene, 5,5-dimethyl-1,2-dipr	0.16	23087	0.001422	2.16841E-11	0.001252	0.125176	0.018058	0.006688	178	13	22	0	0.000101	0.001319	0.001401	0.002232	0	0.015826	0.000117464	0.002232	0
aromatic	136.014		Napthalene, 1,3-dimethyl-	0.19	262906	0.016189	2.93229E-10	0.016927	1.692727	0.244193	0.090442	156	12	12	0	0.001565	0.018784	0.019961	0.018784	0	0.225409	0.00167304	0.018784	0
phenol	136.788		Benzeneacetaldehyde, 2-methoxy-alpha, 5-	0.19	133704	0.008233	1.49125E-10	0.008609	0.860857	0.124187	0.045995	178	11	14	2	0.000698	0.007674	0.008155	0.009768	0.001395	0.092094	0.000683544	0.009768	0.022326
aromatic	137.12		Napthalene, 1,3-dimethyl-'	0.16	71853	0.004424	6.74867E-11	0.003896	0.389581	0.056201	0.020815	156	12	12	0	0.00036	0.004323	0.004594	0.004323	0	0.051878	0.00038505	0.004323	0
aromatic	137.422		Napthalene, 1,4-dimethyl-	0.19	76361	0.004702	8.51684E-11	0.004917	0.491652	0.070926	0.026269	156	12	12	0	0.000455	0.005456	0.005798	0.005456	0	0.06547	0.000485934	0.005456	0

phenol	132.129		2-ethyl-5-n-propylphenol-	0.19	168173	0.010355	1.8757E-10	0.010828	1.082786	0.156203	0.057853	164	11	16	1	0.000952	0.010477	0.011133	0.015239	0.000952	0.125724	0.000933156	0.015239	0.015239
phenol	133.048		2-ethyl-5-n-propylphenol-'	0.19	145316	0.008948	1.62077E-10	0.009356	0.935621	0.134973	0.04999	164	11	16	1	0.000823	0.009053	0.00962	0.013168	0.000823	0.108637	0.000806328	0.013168	0.013168
phenol	133.845		Propofol	0.19	18561	0.001143	2.07018E-11	0.001195	0.119505	0.01724	0.006385	178	12	18	1	9.69E-05	0.001162	0.001235	0.001743	9.69E-05	0.013947	0.000103517	0.001743	0.00155
aromatic	134.552		Napthalene	0.19	222905	0.013726	2.48615E-10	0.014352	1.435179	0.207039	0.076681	156	12	12	0	0.001327	0.015926	0.016924	0.015926	0	0.191113	0.001418488	0.015926	0
aromatic	135.06		1,3-cyclopentadiene, 5,5-dimethyl-1,2-dipr	0.16	23087	0.001422	2.16841E-11	0.001252	0.125176	0.018058	0.006688	178	13	22	0	0.000101	0.001319	0.001401	0.002232	0	0.015826	0.000117464	0.002232	0
aromatic	136.014		Napthalene, 1,3-dimethyl-	0.19	262906	0.016189	2.93229E-10	0.016927	1.692727	0.244193	0.090442	156	12	12	0	0.001565	0.018784	0.019961	0.018784	0	0.225409	0.00167304	0.018784	0
phenol	136.788		Benzeneacetaldehyde, 2-methoxy-alpha, 5-	0.19	133704	0.008233	1.49125E-10	0.008609	0.860857	0.124187	0.045995	178	11	14	2	0.000698	0.007674	0.008155	0.009768	0.001395	0.092094	0.000683544	0.009768	0.022326
aromatic	137.12		Napthalene, 1,3-dimethyl-'	0.16	71853	0.004424	6.74867E-11	0.003896	0.389581	0.056201	0.020815	156	12	12	0	0.00036	0.004323	0.004594	0.004323	0	0.051878	0.00038505	0.004323	0
aromatic	137.422		Napthalene, 1,4-dimethyl-	0.19	76361	0.004702	8.51684E-11	0.004917	0.491652	0.070926	0.026269	156	12	12	0	0.000455	0.005456	0.005798	0.005456	0	0.06547	0.000485934	0.005456	0
phenol	138.008		Propanol, 2-(4-ethoxyphenyl)-2-methyl-	0.19	39401	0.002426	4.39455E-11	0.002537	0.253684	0.036596	0.013554	192	12	16	2	0.000191	0.002287	0.002431	0.00305	0.000381	0.027447	0.000203721	0.00305	0.006099
aromatic	138.655		4,6,8-trimethylazulene	0.19	294678	0.018145	3.28666E-10	0.018973	1.897292	0.273703	0.101372	170	13	14	0	0.00161	0.02093	0.022241	0.02254	0	0.251163	0.001864195	0.02254	0
aromatic	139.253		Napthalene, 1,6,7-trimethyl-	0.19	150296	0.009255	1.67631E-10	0.009677	0.967685	0.139598	0.051703	170	13	14	0	0.000821	0.010675	0.011344	0.011496	0	0.128102	0.000950804	0.011496	0
aromatic	142.896		Napthalene, 2,3,6-trimethyl-	0.19	245	1.51E-05	2.73258E-13	1.58E-05	0.001577	0.000228	8.43E-05	170	13	14	0	1.34E-06	1.74E-05	1.85E-05	1.87E-05	0	0.000209	1.54992E-06	1.87E-05	0
aromatic	143.101		Fluorene	0.12	106404	0.006552	7.49536E-11	0.004327	0.432685	0.062419	0.023118	166	13	10	0	0.000376	0.004888	0.005194	0.00376	0	0.058659	0.000435382	0.00376	0
aromatic	144.014		Napthalene, 1-methyl-7-(methylethyl)-	0.19	949	5.84E-05	1.05846E-12	6.11E-05	0.00611	0.000881	0.000326	184	14	16	0	4.79E-06	6.71E-05	7.13E-05	7.66E-05	0	0.000805	5.97346E-06	7.66E-05	0
aromatic	145.639		Napthalene, 1,2,3,4-tetramethyl	0.19	868	5.34E-05	9.68114E-13	5.59E-05	0.005589	0.000806	0.000299	184	14	16	0	4.38E-06	6.13E-05	6.52E-05	7.01E-05	0	0.000736	5.4636E-06	7.01E-05	0
aromatic	155.596		Napthalene, 1,2,3,4-tetramethyl'	0.17	138145	0.008506	1.3786E-10	0.007958	0.795824	0.114806	0.042521	184	14	16	0	0.000624	0.008735	0.009282	0.009983	0	0.104822	0.000778019	0.009983	0
aromatic	158.69		Napthalene, 1-methyl-7-(methylethyl)-'	0.19	548	3.37E-05	6.11206E-13	3.53E-05	0.003528	0.000509	0.000189	184	14	16	0	2.77E-06	3.87E-05	4.12E-05	4.43E-05	0	0.000465	3.44937E-06	4.43E-05	0
aromatic	159.759		1,4,5,8-tetramethylnapthalene	0.14	39	2.4E-06	3.20513E-14	1.85E-06	0.000185	2.67E-05	9.89E-06	184	14	16	0	1.45E-07	2.03E-06	2.16E-06	2.32E-06	0	2.44E-05	1.80883E-07	2.32E-06	0
aromatic	161.705		Napthalene, 1,2,3,4-tetramethyl''	0.19	0	0	0	0	0	0	0	184	14	16	0	0	0	0	0	0	0	0	0	0
aromatic	162.563		1,4,5,8-tetramethylnapthalene'	0.19	124	7.64E-06	1.38302E-13	7.98E-06	0.000798	0.000115	4.27E-05	184	14	16	0	6.26E-07	8.76E-06	9.31E-06	1E-05	0	0.000105	7.80515E-07	1E-05	0
aromatic	164.599		2-methyl-3-biphenylmethanol	0.19	7073	0.000436	7.88879E-12	0.000455	0.04554	0.00657	0.002433	198	14	14	1	3.32E-05	0.000465	0.000494	0.000465	3.32E-05	0.005574	4.13729E-05	0.000465	0.000531
aromatic	165.843		1,4,5,8-tetramethylnapthalene''	0.19	0	0	0	0	0	0	0	184	14	16	0	0	0	0	0	0	0	0	0	0
aromatic	167.753		Azulene, 1,4-dimethyl-7-methylethyl-	0.14	0	0	0	0	0	0	0	198	15	18	0	0	0	0	0	0	0	0	0	0
aromatic	169.136		1,1-biphenyl,3,4-diethyl-	0.19	0	0	0	0	0	0	0	210	16	18	0	0	0	0	0	0	0	0	0	0
																	0.941061	1			11.29273	0.083817506		
					16239985		1.73229E-08	1	100	14.426	5.342963						C(mol)		H(mol)	O(mol)	C(weight)		H(weight)	O(weight)
																	0.941061		1.272814	0.109243	11.29273		1.272814	1.747891
																	O/C (mol)		0.116085		C(%)		H(%)	O(%)
																	H/C (mol)		1.35253		78.89602		8.892439	12.21154

	Weight distributi on	
Aromatic Hydrocarbon	0.145923	14.59%
Aliphatic Hydrocarbon	0	0.00%
Phenolics	0.627075	62.71%
cyclo oxygenates	0.110625	11.06%
ketones	0.103786	10.38%
Aliphatic Acid	0.000339	0.03%
Aliphatic Alcohal	0	0.00%
Aliphatic Aldehyde	0	0.00%
Furan derivative	0.004448	0.44%
Sugar	0	0.00%
	0.992197	

		aromatic	aliphatic h	phenol	cyclo oxy	ketone	furan	sugar	aliphatic acid	aliphatic alcohal	aliphatic aldehyde			
1	C1	0	0	0	0	0	0	0	0	0	0		C1	0
2	C2	0	0	0	0	0	0	0	0.000173283	0	0		C2	0.000173
3	C3	0	0	0	0	0.013844	0	0	0	0	0		C3	0.013844
4	C4	0	0	0	0	0.020033	0	0	0	0	0		C4	0.020033
5	C5	0.000325	0	0	0.035032	0.023662	0	0	0	0	0		C5	0.059019
6	C6	0	0	0.054887	0.044882	0.018225	0	0	0	0	0		C6	0.117994
7	C7	0.004637	0	0.11299	0.014325	0.011382	0	0	0	0	0		C7	0.143334
8	C8	0.006614	0	0.160871	0.004557	0.004166	0	0	0	0	0		C8	0.176207
9	C9	0.036577	0	0.101234	0.001106	0	0.004194	0	0	0	0		C9	0.143111
10	C10	0.023706	0	0.135583	0	0	0	0	0	0	0		C10	0.159289
11	C11	0	0	0.06192	0.003971	0	0	0	0	0	0		C11	0.065891
12	C12	0.047275	0	0.003666	0	0	0	0	0	0	0		C12	0.050941
13	C13	0.040199	0	0	0	0	0	0	0	0	0		C13	0.040199
14	C14	0.009965	0	0	0	0	0	0	0	0	0		C14	0.009965
15	C15	0	0	0	0	0	0	0	0	0	0		C15	0
16	C16	0	0	0	0	0	0	0	0	0	0		C16	0
17	C17	0	0	0	0	0	0	0	0	0	0		C17	0
														1

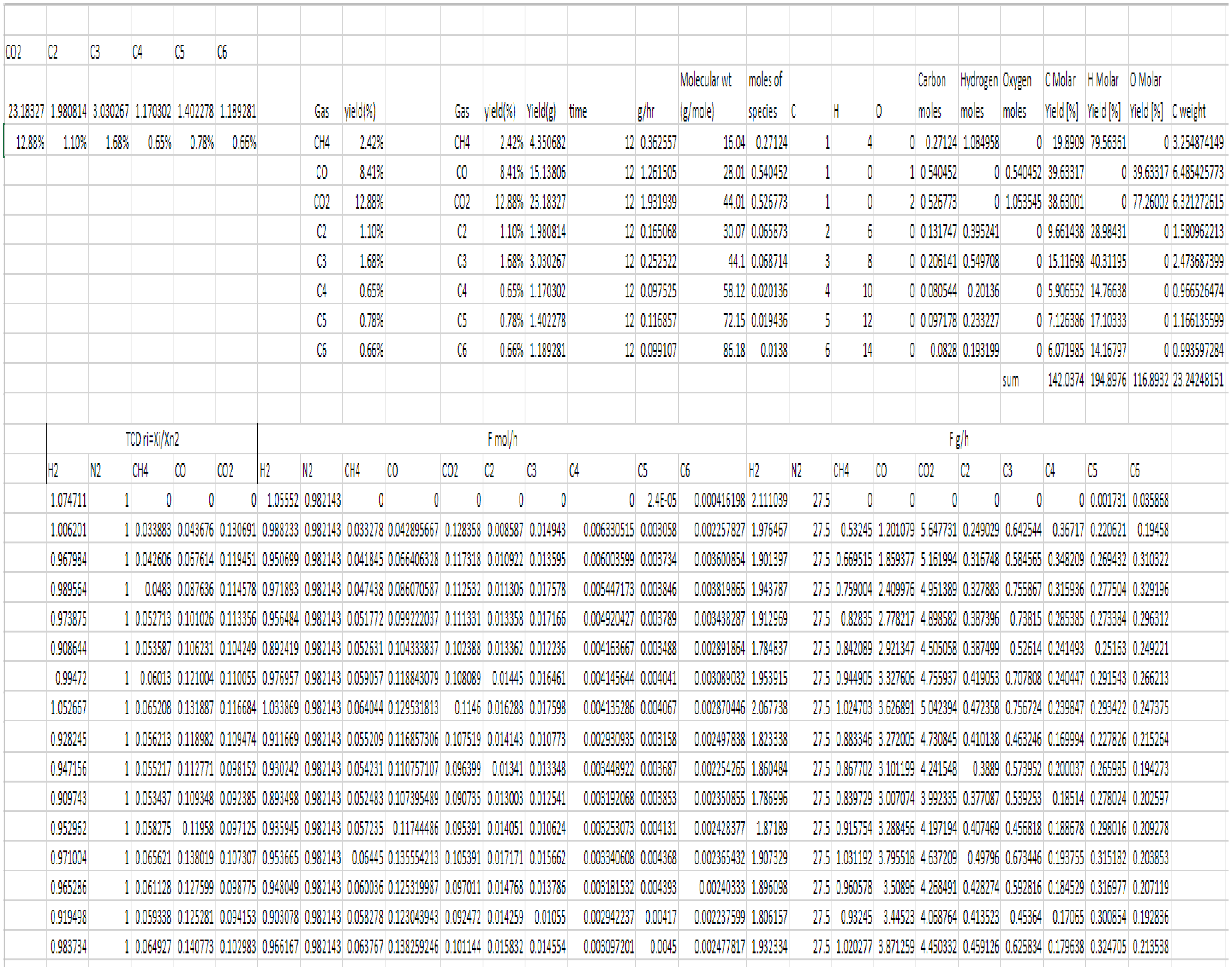


Species	TCD Eq Coef	TCD rf	K =fi/fn2	g/mol
H2	27.25	0.0367	23.97798165	2
N2	653.4	0.0015	1	28
CH4	726	0.0014	0.9	16
CO	890	0.0011	0.734157303	28
CO2	1194	0.0008	0.547236181	44

Species	FID eq coef	FID rf	K=fi/Fmet	g/mol
Methane	1951.85	0.000512334	1.00	16
Ethane	3494	0.000286205	0.56	30
Ethene	3666	0.000272777	0.53	28
Propane	5570	0.000179533	0.35	44
Propene	5500	0.000181818	0.35	42
Butane	7314	0.000136724	0.27	58
i/x-butane	7314	0.000136724	0.27	58
Pentane	9130	0.000109529	0.21	72.15
Hexane	11032	9.06454E-05	0.18	86.18

gas sampling interval [h]	0.333333333			
Feed rate [g/h]	36		CH4	CO
duration	5	yield [g]	4.3506818	15.13806
total biomass	180	yield [g/gbio]	2.42%	8.41%
total gas yield [g]	51.444956			
total gas yield [g/gbio]	28.58%			
				1.38
				7.15
				7.09
				0.66
				1.17

Experiments		duration [hours]	H2 Flow [l/min]	N2 Flow [l/min]	hopper N2 [l/h]	total N2 [l/min]	H2	N2	CH4	CO	CO2	Methane	Ethane	Ethene	Propane	Propene	Butane	Pentane	Hexane
					Average Area				Average TCD Area						FID Area				
	1	0	0.8	0.2	10	0.366666667	713.6	15921.2	0	0	0	24.1	0	6.8	0	33.7	22.3	14.9	310.2
	2	0.333333333	0.8	0.2	10	0.366666667	601.9	14343.4	540	853.3	3425.5	4133.8	0	2133.4	30	5538.6	3145.5	1899.2	1682.8
	3	0.666666667	0.8	0.2	10	0.366666667	587.9	14562.9	689.4	1341.2	3178.8	5292.1	6.1	2756.6	405	4752.9	3037.1	2361.4	2732.4
	4	1	0.8	0.2	10	0.366666667	580.9	14075.7	755.4	1680.2	2947.1	5850.5	21.2	2995.9	809.8	3785.6	2687.2	2351.1	2802
	5	1.333333333	0.8	0.2	10	0.366666667	570.5	14046.4	822.7	1932.9	2909.6	6329.4	42.2	3224.1	1053.4	3058.6	2406.2	2316.2	2522.1
	6	1.666666667	0.8	0.2	10	0.366666667	572.1	15097	898.9	2184.5	2876	6914	62.1	3448.6	1100	2591	2187.9	2290.8	2279.4
	7	2	0.8	0.2	10	0.366666667	571	13764.1	919.6	2268.6	2768.1	7071.8	72.5	3514.4	1106.1	2350.5	1985.7	2312.3	2121.2
	8	2.333333333	0.8	0.2	10	0.366666667	572.9	13049.7	945.5	2344.3	2782.5	7329.7	79.9	3648.4	1106.4	2301.3	1893.1	2327.2	1971.1
	9	2.666666667	0.8	0.2	10	0.366666667	552	14259	890.6	2310.9	2852.5	6868.8	115.9	3403.2	1096.2	2001.8	1458.6	1964.3	1864.6
	10	3	0.8	0.2	10	0.366666667	564	14278.1	876	2193.2	2560.9	6743.7	76.2	3296.3	1009.1	2043.2	1715.5	2395	1757.4
	11	3.333333333	0.8	0.2	10	0.366666667	565.2	14896.9	884.5	2218.8	2514.9	6819.2	76.8	3302.2	991.2	1972.1	1659	2503.4	1832.7
	12	3.666666667	0.8	0.2	10	0.366666667	563.4	14176	917.9	2309	2516	7115.9	85.1	3408.7	1007.2	1939.7	1617.8	2567.7	1811.5
	13	4	0.8	0.2	10	0.366666667	555.9	13727.4	1000.9	2580.7	2691.8	7700.7	111.8	3771.2	1081.9	1931.7	1596.6	2651.2	1722.7
	14	4.333333333	0.8	0.2	10	0.366666667	561.6	13950.3	947.5	2424.6	2518	7287.2	99.1	3486	1016.3	1831.5	1544.7	2666.3	1750.3
	15	4.666666667	0.8	0.2	10	0.366666667	561.8	14650.2	965.9	2500	2520.6	7436.7	105.7	3533.5	1039.6	1834.4	1501.8	2660.5	1713.2
	16	5	0.8	0.2	10	0.366666667	560	13649.7	984.7	2617.3	2568.7	7585.9	117.3	3649.5	1038	1792.5	1473.8	2676.9	1768.6



CO2	C2	C3	C4	C5	C6
23.18327	1.980814	3.030267	1.170302	1.402278	1.189281
12.88%	1.10%	1.68%	0.65%	0.78%	0.66%

Gas	yield(%)
CH4	2.42%
CO	8.41%
CO2	12.88%
C2	1.10%
C3	1.68%
C4	0.65%
C5	0.78%
C6	0.66%

Gas	yield(%)	Yield(g)	time	g/hr	Molecular wt (g/mole)	moles of species	C	H	O	Carbon moles	Hydrogen moles	Oxygen moles	C Molar Yield [%]	H Molar Yield [%]	O Molar Yield [%]	C weight
CH4	2.42%	4.350682	12	0.362557	16.04	0.27124	1	4	0	0.27124	1.084958	0	19.8909	79.56361	0	3.254874149
CO	8.41%	15.13806	12	1.261505	28.01	0.540452	1	0	1	0.540452	0	0.540452	39.63317	0	39.63317	6.485425773
CO2	12.88%	23.18327	12	1.931939	44.01	0.526773	1	0	2	0.526773	0	1.053545	38.63001	0	77.26002	6.321272615
C2	1.10%	1.980814	12	0.165068	30.07	0.065873	2	6	0	0.131747	0.395241	0	9.661438	28.98431	0	1.580962213
C3	1.68%	3.030267	12	0.252522	44.1	0.068714	3	8	0	0.206141	0.549708	0	15.11698	40.31195	0	2.473687399
C4	0.65%	1.170302	12	0.097525	58.12	0.020136	4	10	0	0.080544	0.20136	0	5.906552	14.76638	0	0.966526474
C5	0.78%	1.402278	12	0.116857	72.15	0.019436	5	12	0	0.097178	0.233227	0	7.126386	17.10333	0	1.166135599
C6	0.66%	1.189281	12	0.099107	86.18	0.0138	6	14	0	0.0828	0.193199	0	6.071985	14.16797	0	0.993597284
												sum	142.0374	194.8976	116.8932	23.24248151

TCD ri=Xi/Xn2					F mol/h										F g/h									
H2	N2	CH4	CO	CO2	H2	N2	CH4	CO	CO2	C2	C3	C4	C5	C6	H2	N2	CH4	CO	CO2	C2	C3	C4	C5	C6
1.074711	1	0	0	0	1.05552	0.982143	0	0	0	0	0	0	2.4E-05	0.000416198	2.111039	27.5	0	0	0	0	0	0	0.001731	0.035868
1.006201	1	0.033883	0.043676	0.130691	0.988233	0.982143	0.033278	0.042895667	0.128358	0.008587	0.014943	0.006330515	0.003058	0.002257827	1.976467	27.5	0.53245	1.201079	5.647731	0.249029	0.642544	0.36717	0.220621	0.19458
0.967984	1	0.042606	0.067614	0.119451	0.950699	0.982143	0.041845	0.066406328	0.117318	0.010922	0.013595	0.006003599	0.003734	0.003600854	1.901397	27.5	0.669515	1.859377	5.161994	0.316748	0.584565	0.348209	0.269432	0.310322
0.989564	1	0.0483	0.087636	0.114578	0.971893	0.982143	0.047438	0.086070587	0.112532	0.011306	0.017578	0.005447173	0.003846	0.003819865	1.943787	27.5	0.759004	2.409976	4.951389	0.327883	0.755867	0.315936	0.277504	0.329196
0.973875	1	0.052713	0.101026	0.113356	0.956484	0.982143	0.051772	0.099222037	0.111331	0.013358	0.017166	0.004920427	0.003789	0.003438287	1.912969	27.5	0.82835	2.778217	4.898582	0.387396	0.73815	0.285385	0.273384	0.296312
0.908644	1	0.053587	0.106231	0.104249	0.892419	0.982143	0.052631	0.104333837	0.102388	0.013362	0.012236	0.004163667	0.003488	0.002891864	1.784837	27.5	0.842089	2.921347	4.505058	0.387499	0.52614	0.241493	0.25163	0.249221
0.99472	1	0.06013	0.121004	0.110055	0.976957	0.982143	0.059057	0.118843079	0.108089	0.01445	0.016461	0.004145644	0.004041	0.003089032	1.953915	27.5	0.944905	3.327606	4.755937	0.419053	0.707808	0.240447	0.291543	0.266213
1.052667	1	0.065208	0.131887	0.116684	1.033869	0.982143	0.064044	0.129531813	0.1146	0.016288	0.017598	0.004135286	0.004067	0.002870446	2.067738	27.5	1.024703	3.626891	5.042394	0.472358	0.756724	0.239847	0.293422	0.247375
0.928245	1	0.056213	0.118982	0.109474	0.911669	0.982143	0.055209	0.116857306	0.107519	0.014143	0.010773	0.002930935	0.003158	0.002497838	1.823338	27.5	0.883346	3.272005	4.730845	0.410138	0.463246	0.169994	0.227826	0.215264
0.947156	1	0.055217	0.112771	0.098152	0.930242	0.982143	0.054231	0.110757107	0.096399	0.01341	0.013348	0.003448922	0.003687	0.002254265	1.860484	27.5	0.867702	3.101199	4.241548	0.3889	0.573952	0.200037	0.265985	0.194273
0.909743	1	0.053437	0.109348	0.092385	0.893498	0.982143	0.052483	0.107395489	0.090735	0.013003	0.012541	0.003192068	0.003853	0.002350855	1.786996	27.5	0.839729	3.007074	3.992335	0.377087	0.539253	0.18514	0.278024	0.202597
0.952962	1	0.058275	0.11958	0.097125	0.935945	0.982143	0.057235	0.11744486	0.095391	0.014051	0.010624	0.003253073	0.004131	0.002428377	1.87189	27.5	0.915754	3.288456	4.197194	0.407469	0.456818	0.188678	0.298016	0.209278
0.971004	1	0.065621	0.138019	0.107307	0.953665	0.982143	0.06445	0.135554213	0.105391	0.017171	0.015662	0.003340608	0.004368	0.002365432	1.907329	27.5	1.031192	3.795518	4.637209	0.49796	0.673446	0.193755	0.315182	0.203853
0.965286	1	0.061128	0.127599	0.098775	0.948049	0.982143	0.060036	0.125319987	0.097011	0.014768	0.013786	0.003181532	0.004393	0.00240333	1.896098	27.5	0.960578	3.50896	4.268491	0.428274	0.592816	0.184529	0.316977	0.207119
0.919498	1	0.059338	0.125281	0.094153	0.903078	0.982143	0.058278	0.123043943	0.092472	0.014259	0.01055	0.002942237	0.00417	0.002237599	1.806157	27.5	0.93245	3.44523	4.068764	0.413523	0.45364	0.17065	0.300854	0.192836
0.983734	1	0.064927	0.140773	0.102983	0.966167	0.982143	0.063767	0.138259246	0.101144	0.015832	0.014554	0.003097201	0.0045	0.002477817	1.932334	27.5	1.020277	3.871259	4.450332	0.459126	0.625834	0.179638	0.324705	0.213538

Risk Assessment:

ID	48769	**Status**	**Date**
Risk Area	Risikovurdering: Helse, miljø og sikkerhet (HMS)	Created	16.06.2022
Created by	Hammad Ali	Assessment started	05.07.2022
Responsible	Hammad Ali	Measures decided	
		Closed	

Risk Assessment:

CAT, Master Student, 2022, HAMMAD ALI

Valid from-to date:
6/16/2022 - 6/16/2025

Location:
IKP

Goal / purpose

The reason for this risk assessment is to identify potential hazards during lab work dealing with chemicals and how to reduce the risks by analyzing them during lab work. For my project, bio-oil production from bio-mass using thermochemical pyrolysis technique. The reactor used for this purpose is fluidized bed which holds fluidizing medium and there is a fixed bed reactor also which holds an upgrading catalyst to upgrade the pyrolysis vapors to produce upgraded bio-oil. To get the desirable yield of bio-oil, an upgrading catalyst is used to convert other compounds into bio-oil without changing other components of product. The distribution is not uniform and therefore should be done with great care.

Background

The project based on fast pyrolysis of bio-mass to make bio-oil along with gases and some char. The rig used for this purpose is 1.10 in hall D first floor. Along with rig we need to use few lab equipment like sample vials and analyzers to do sample analysis.

Biomass used is in the range of max 1000 micrometer.
I also need to use GC FID/TCD for gas analysis and GC FID for liquid analysis along with GC MS analyzer to analyze samples for retention time data for coming out after the reaction.
And Karl Fischer titrator for water content analysis. The principle for this titration is based on oxidation reaction and an end point is achieved when all water is consumed.

Chemicals used are:
N_2
H_2
Ethyl alcohol
GVL (solvent)
Acetone (for cleaning)
Catalyst(Ru/TiO_2, ZSM-5, FCC, Pt on TiO_2). Currently I am only using Ru/TiO_2.
Ice for secondary condensers.

There might be characterization techniques used for catalysts preparation so it is not certain that it will happen and it will be accessed at that time but now nothing from characterization for catalysts required. the techniques will be BET, XRD, TEM.

Description and limitations

Biomass pre-treatment.
As biomass is the main raw material for our process, it needed to be treated before feeding into the rig. The moisture content should be under certain range and for this drying oven at 150oC is used to dry out the moisture from biomass. The biomass placed for at least 8 hours in there.

Rig Operation 1.10:

It is the fluidized bed setup for the pyrolysis of biomass which consists of a fluidized bed reactor (reactor 01), feeder for feeding the biomass particles (250 to 500µm), filter for removing the char, upgrading reactor (Reactor 02) and condensing unit for separating the Bio-oil and Non-condensable gases.

Leak test before experiment:

Before starting new experiment we need to clean up the plant with residues left from the previous experiments. Steps below explained:

1. First we need to clean the fluidized reactor by opening the joints with the help of ranch and remove all the used material which is sand and then we need to refill it from the top of the reactor with funnel. By opening the coupling between the fluidized bed reactor and the safety release valve above the reactor, fluidizing materials will be added with the help of a funnel. Further, it is again connected tightly as it was before. The valve at the top of the reactor should be dealt with great care as it is sensitive.

2. After loading the fluidizing media in the pyrolysis reactor, there is a need to load catalyst in the upgrading reactor, so same procedure will be followed for this reactor as well. First we loosen up joints and remove the present catalyst. If the catalyst is in good condition we can reuse it otherwise we have to load new batch of catalyst. The joints should be tightened properly as no gases escapes.

3. After loading catalyst in the upgrading reactor, cleaning for condenser is done because of biooil accumulation at the bottom of the assembly. First we open the joint coming from the upgrading reactor and attach a small pipe for cleaning purpose. For cleaning, acetone is passed with the help of peristaltic pump. It is circulated for several times throughout the condensing unit to remove anything left after the experiment.
After acetone is passed, nitrogen is passed for few minutes to remove any leftover acetone in the pipes.

After these steps, every joints tighten up and then leak test can be done to check potential leak points. Nitrogen is passed at certain pressure and then hold up is checked for it by observing a straight line on PID pc to see if pressure is dropping, leak spray can be used also if there's a leak. For PHT (pressure hold-up test), after tightening all joints, start flowing nitrogen and monitor pressure rise throughout the rig. If it stabilizes around 0.7 bar then it's good to go otherwise check for any leak.

New Experiment:
After leak test, we can move forward to perform new experiment, below steps mentioned:

4. Check the biomass in the feeder. It should be more than 150 grams. It also depends how long the experiment will continue.

5. Heating of the reactor has been done in presence of Nitrogen. For this, first, open the Nitrogen valve and close the air valve so only Nitrogen can flow into the system. Click on the (set config) on the screen and select 'heat' by switching on the manual switches for heating. the setting for the first reactor is 500oC and for the second reactor is 400oC. The filter lines are at 350oC.

6. After the pressure hold-up test, burning of the reactors has been performed with Air. It also cleans the reactor through the combustion of remaining residue in the reactor and pipeline from the earlier experiment. It will take 2 hrs. As it will clean all the residual materials left inside the rig. After heating, open nitrogen around 1 l/min flow and slowly open hydrogen at 1.5 l/min and turn on the feed switch as well. The gas flow can be adjusted accordingly, as of currently I am using 0.8 l/min of H2 and 0.2 l/min of N2. 0.16 l/min of N2 also goes to feeder as well.

7. Switch on the chilling unit for condenser, ethylene glycol is used as coolant and set the temperature, at -10oC. The chiller temperature can be adjusted according to requirement.

8. After switching on the feeder, the feed will flow at 20 gm/hr and the experiment can run as long as possible and till 15 hours. The gases will be analyzed by GC and biooil sample.

Shutdown procedure:
After experiment is completed, the heating turned off and cooling is done with N2 flowing at 1 l/min and the chiller will remain on to rapid cooling process for the rig. The GC TCD/FID also turned off after adjacent sample completes and puts on standby mode. H2 also turns off during that time. The rig cools down in few hours before oil extracted from it.

Bio-oil Collection:

After the experiment, the bio-oil produced collected from the collection pipe form the rig, using a sample vial to collect it directly from the rig. As there are additional condensers, oil samples also collected from them directly and also with acetone if there is viscous liquid in there. and similarly acetone passed through first condenser to wash it for oil left in there.

Bio-oil Analysis:

Karl Fisher Titrator (KS 317).

Karl Fisher Titrator - Karl Fischer titration is a classic titration method in chemical analysis that uses coulometric or volumetric titration to determine trace amounts of water in a sample. It is used to analyze water content in biooil sample.

Do the standardization of the Karl fisher setup before starting.
1. Filter the sample using a 20 μm filter.
2. Dilute the aqueous phase of bio-oil 10 to 15 times with pure ethanol.
3. Take 1 ml of filtered sample or around 50% in a syringe and put it into the titrator and enter the weighed value sample which is put

on the titrator.
4. Press the start button after entering the value of the amount which is entered. It will tell the percentage of water in the sample as RI content.
5. Calculate the mass fraction of water in the initial one by using simple titration formula.

GC analysis:
GC-FID analysis:

The collected aqueous product needed to be analyzed for components. For this purpose take a clean vial and fill it with aqueous product after filtering it with 20 micrometer filter. Take the vials and place it at 9th or 10th position in the analyzer. Start analysis by selecting the method which is already in the system. Keep an eye on the temperature for 250°C.

GC-TCD\FID online analysis for gases:
This will be done simultaneously when the experiment is going on and we can start the analysis by naming the sample according to the date and name of catalyst. The sample will be analyzed continuously after every 20 minutes. The gases will be analyzed will be pyrolysis vapors including Carbon monoxide, Carbon Dioxide, Hydrogen, Methane and Nitrogen and other concentrations.

GC-MS for compounds detection:
GC-MS also used few times for updating library method for GC FID for oil analysis. Similar analogy followed to run samples on GC-MS like in GC FID. Samples in GC vials can be used for the purpose as well.

Catalyst preparation.
1. As Ru/TiO2 was prepared by using TiO2 pellets which are commercially available so titania pellets were calcined using calcination oven. The setting was managed accordingly.
2. After calcination of titania, Ru solution made with RuCl3 in water based on calculations done with the help of magnetic stirrer.
3. For impregnation, lab 321 is used with impregnation unit for it. N2 also used to make fine droplets to cover titania surface. After all the solution been injected on pellets give it few minutes to cover up all the liquid solution.
4. After impregnation, catalyst placed in drying oven to remove the moisture gained during the solution injection, it can stay there for 8 hours at least before calcination is done on it.

Catalyst calcination.
Calcination will be performed at 350 to 400°C in presence of Air (90% Nitrogen +10% Oxygen) for few hours to remove the impurities through oxidation such as Nitrogen Dioxide, Chloride and other Nitric compounds.
Calcination was done on pure titania and after impregnation as well.

Rotary Evaporator Use.
Rotary evaporator is being used to separate out acetone used in the cleaning of condensers and to collect bio oil for mass balance and to reuse acetone again for cleaning of condensers.
The procedure for using rotary evaporator is explained below:
1. First check all the connections as there is vacuum pump attached and cooling water lines are also connected to condenser.
2. Fill up the heating bath with water and set the temperature at a desired set point.
3. Attach round bottom flasks to the vacuum pump and at the bottom of condenser for collecting acetone.
4. Fill up acetone with bio oil in round bottom flask which will be attached to side of condenser and dipped in heating bath.
5. Turn on the flow of cooling water and let it for few minutes.
6. Check that release valves are closed so vacuum can be achieved.
7. After checking all things mentioned above, start the rotation of flask with acetone at a slow rate and increase it eventually.
8. After all the acetone is separated out and no more is condensing, stop the rotation and let it rest for few minutes.
9. Release the vacuum by opening valves from condenser and turning off the vacuum pum.
10. Collect the acetone from both flasks in the bottle and let it rest in vacuum hood to dry.
11. The flask with bio oil, wash it with acetone and after cleaning it, let it rest to dry out.
12. Throw away water and stop cooling water flow.

Note about THF:
I am not using THF for any purpose now either during experiment or for analysis part.

Prerequesites, assumptions and simplifications

Will attach safety data sheets for the gases and chemicals used during experimentation.
The gases like H2 and N2 can be dangerous at high pressure and temperature so we have to be careful with them. Also we are using air (oxygen primarily) so we need to consider that as well.
We need to avoid liquid going in to GC analyzer in order to save from trouble because then we have to make a lot of work cleaning and it can damage the GC analyzer as well as it is designed for gases.
We use ethanol for titration and it is flammable and it can be dangerous for health so we need to be careful with it.
Same things goes with acetone. It is flammable and it can cause skin problems. So using PPE's are important.
Using air at high temperature should be monitored continuously.
Great care should be taken while using GVL,THF and any other solvents as they are highly volatile and have high health hazards. Also THF will no longer be used for experimentation purposes but as it was used previously so it is necessary to have it under consideration. Wear gloves, glasses and lab coat while working with solvents and for THF, peroxide formation is also a situation and should not be kept openly in lab and peroxide testing is necessary on regualr basis. If THF is not being used for long time, it should be disposed off properly.

Attachments

Nitrogen, compressed_Biogon N_1.2 ENNO_tcm639-445696.pdf
Hydrogen, compressed_1.1_ENNO_tcm639-445168.pdf
ETHANOL AHYD HISTO 4L.pdf
msds-acetone.pdf
ETHYLENE GLYCOL LABORATORY 4L.pdf
34816-500ML_SDS_JP_E.pdf
ghs_34738.pdf
CN15373144.pdf
MicrosoftTeams-image.png

References

[Ingen registreringer]

Summary, result and final evaluation

The summary presents an overview of hazards and incidents, in addtition to risk result for each consequence area.

Hazard: **Chemical usage during titration.**

Incident: **Ethanol spillage while using it for titration.**

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟡	Risiko after measures:	⚪

Incident: **Hydranal ketosolver from titrator can be spilled while working.**

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢	Risiko after measures:	⚪

Incident: **Syringe usage with needle**

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪

Incident: **Spillage of chemicals on weigh scale.**

Consequence area:	Materielle verdier	Risk before measures:	🟢	Risiko after measures:	⚪

Hazard: **Running Experiment on Rig**

Incident: **Using acetone for vials and flask cleaning and for cleaning of condenser on rig.**

Consequence area:	Helse	Risk before measures:	🟢	Risiko after measures:	⚪
	Materielle verdier	Risk before measures:	🟡	Risiko after measures:	⚪

Incident: **Gas Leakage from rig pipes**

Consequence area:	Helse	Risk before measures:	🟢	Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢	Risiko after measures:	⚪

Hazard: **Running Experiment on Rig**

Incident: **Gas Leakage from rig pipes**

	Materielle verdier	Risk before measures:	🟡	Risiko after measures:	⚪

Incident: **Pressure and temperature rise during experiment.**

Consequence area:	Materielle verdier	Risk before measures:	🟢	Risiko after measures:	⚪

Incident: **Glassware are fragile**

Not to be analyzes.

Hazard: **Rotary Evaporator usage**

Incident: **Cooling water leakage.**

Consequence area:	Materielle verdier	Risk before measures:	🟡	Risiko after measures:	⚪

Incident: **Acetone spillage.**

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢	Risiko after measures:	⚪

Final evaluation

Organizational units and people involved

A risk assessment may apply to one or more organizational units, and involve several people. These are lsited below.

Organizational units which this risk assessment applies to

- Institutt for kjemisk prosessteknologi

Participants

De Chen
Kumar Ranjan Rout
Petter Tingelstad

Readers

Estelle Marie M. Vanhaecke

Björn Frederik Baumgarten

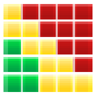
Robert Lennard Peters

Others involved/stakeholders

[Ingen registreringer]

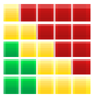
The following accept criteria have been decided for the risk area Risikovurdering: Helse, miljø og sikkerhet (HMS):

Helse



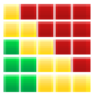
🟨	🟥	🟥	🟥	🟥
🟨	🟨	🟥	🟥	🟥
🟩	🟨	🟨	🟥	🟥
🟩	🟩	🟨	🟨	🟥
🟩	🟩	🟨	🟨	🟨

Materielle verdier



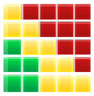
🟨	🟥	🟥	🟥	🟥
🟨	🟨	🟥	🟥	🟥
🟩	🟨	🟨	🟥	🟥
🟩	🟩	🟨	🟨	🟥
🟩	🟩	🟨	🟨	🟨

Omdømme



🟨	🟥	🟥	🟥	🟥
🟨	🟨	🟥	🟥	🟥
🟩	🟨	🟨	🟥	🟥
🟩	🟩	🟨	🟨	🟥
🟩	🟩	🟨	🟨	🟨

Ytre miljø



🟨	🟥	🟥	🟥	🟥
🟨	🟨	🟥	🟥	🟥
🟩	🟨	🟨	🟥	🟥
🟩	🟩	🟨	🟨	🟥
🟩	🟩	🟨	🟨	🟨

Overview of existing relevant measures which have been taken into account

The table below presents existing measures which have been take into account when assessing the likelihood and consequence of relevant incidents.

Hazard	Incident	Measures taken into account
Chemical usage during titration.	Ethanol spillage while using it for titration.	
	Hydranal ketosolver from titrator can be spilled while working.	
	Syringe usage with needle	
	Spillage of chemicals on weigh scale.	
Running Experiment on Rig	Using acetone for vials and flask cleaning and for cleaning of condenser on rig.	
	Gas Leakage from rig pipes	
	Pressure and temperature rise during experiment.	
Rotary Evaporator usage	Cooling water leakage.	
	Acetone spillage.	

Existing relevant measures with descriptions:

PPE Usage

It is required to have lab coat and goggles all the time while working in the lab.

SDS Implementation

Read through SDS of gases and chemicals and take care accordingly.

Procedure

Developed procedure both for experimentation and for result analysis. Take great care while dealing with chemicals and while using rig for experimentation.

Instruments training

Having instruments training will be more useful while performing lab experiments and during result analysis as it will save time and will be good to reduce chances of having incident.

Emergency shut down

There is an emergency shut down procedure which can be practiced in case of an emergency or something comes up.

Fire Alarms

There are fire alarms installed throughout the department. In labs there are also alarms which will be activated in case of emergency.

Ventilation

The buildings and labs have ventilation for proper circulation of air and to remove vapors in air. It is very important that ventilation should be on all the time otherwise the air will be having more concentration of different vapors in the facility.

Risk analysis with evaluation of likelihood and consequence

This part of the report presents detailed documentation of hazards, incidents and causes which have been evaluated. A summary of hazards and associated incidents is listed at the beginning.

The following hazards and incidents has been evaluated in this risk assessment:

- **Chemical usage during titration.**
  - Ethanol spillage while using it for titration.
  - Hydranal ketosolver from titrator can be spilled while working.
  - Syringe usage with needle
  - Spillage of chemicals on weigh scale.
- **Running Experiment on Rig**
  - Using acetone for vials and flask cleaning and for cleaning of condenser on rig.
  - Gas Leakage from rig pipes
  - Pressure and temperature rise during experiment.
- **Rotary Evaporator usage**
  - Cooling water leakage.
  - Acetone spillage.

Detailed view of hazards and incidents:

Hazard: Chemical usage during titration.

Chemicals using during titration and present on titrator can be spilled and there are hazards present which need to be safeguarded.

Incident: Ethanol spillage while using it for titration.

During titration, ethanol can be spilled on skin and on to the shelve and can cause serious health issues as it is strong skin irritant. It is highly flammable liquid and can cause serious damage to lab facility as well.

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

Can use PPE's to protect skin and can handle ethanol with care to avoid spillage.

Consequence area: Helse

Assessed consequence: **Large (3)**

Comment: Skin irritation can cause serious problems

Risk:

Consequence area: Ytre miljø

Assessed consequence: **Very large (4)**

Comment: If ethanol catches fire it can damage the laboratory big time and fire can spread easily to nearby buildings.

Risk:

Incident: Hydranal ketosolver from titrator can be spilled while working.

Hydranal ketosolver can cause skin problems and it is highly flammable as well. It's vapors can cause dizziness as well.

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

Can be protected if handled properly.

Consequence area: Helse

Assessed consequence: **Large (3)**

Comment: The vapors can cause dizziness if inhaled and it can cause strong skin irritation and to eyes as well. It can be saved by PPE's and lab glasses while dealing with chemical

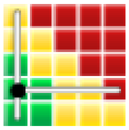
Risk:

Consequence area: Ytre miljø

Assessed consequence: **Small (1)**

Comment: As it is flammable and it is attached to an electronic instrument so it can be dangerous being a flammable chemical but proper handling of the chemical can reduce this risk.

Risk:



Incident: Syringe usage with needle

Using syringe to load sample on titrator and while filling sample in syringe from vial should be done with care.

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

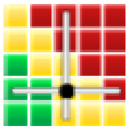
By capping syring needle it can be prevented.

Consequence area: Helse

Assessed consequence: **Large (3)**

Comment: As the likelihood is small, the consequences can large because if syringe needle with chemical touches the skin which has toxic chemicals then it can be a problem so we should take great care and try to cap needle whenever it's not in use.

Risk:



Incident: Spillage of chemicals on weigh scale.

While using weigh scale chemical vials or container can fall off and chemical can be spilled on weighing scale.

Likelihood of the incident (common to all consequence areas): **Unlikely (1)**

Kommentar:

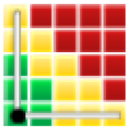
It is very rare that this incident could happen.

Consequence area: Materielle verdier

Assessed consequence: **Small (1)**

Comment: The chemicals will be wasted apart from any damage to any person working there.

Risk:



Hazard: Running Experiment on Rig

There are several steps needed to be done before running experiment. And they are needed to be looked before starting the experiment.

Incident: Using acetone for vials and flask cleaning and for cleaning of condenser on rig.

After experiment we need to clean the condenser to clean any left over bio-oil from the condenser by passing acetone through it using pump.
Similarly vials and flasks used for products needed to be cleaned with acetone.

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

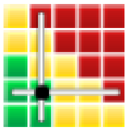
Proper handling and with use of PPE's it can be prevented.

Consequence area: Helse

Assessed consequence: **Medium (2)**

Comment: As small amount of acetone is being used but it still can be dangerous to the worker and to the environment as it is toxic and it causes skin irritation. Along with it, is flammable.

Risk:

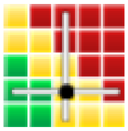


Consequence area: Materielle verdier

Assessed consequence: **Large (3)**

Comment: Acetone use during cleaning on rig can cause problems if it can go to GC analyzer. It can be prevented by closing the gas lines valve and should be double checked as it is very important step because it can damage the equipment.

Risk:



Incident: Gas Leakage from rig pipes

Gases can be leaked while heating or performing experiment. As we need the load sand and catalyst in the reactors so for that purpose we need to loose and tight joints several times and there might be a possibility of leakage from them.

Likelihood of the incident (common to all consequence areas): **Unlikely (1)**

Kommentar:

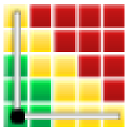
It is checked before starting the experiment that whether joints are properly tightened. The pressure is monitored on PC screen.

Consequence area: Helse

Assessed consequence: **Small (1)**

Comment: As nitrogen is an inert gas so it would not harm worker in case of exposure. But if excess amount amount is exposed it might cause some problem.

Risk:

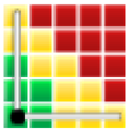


Consequence area: Ytre miljø

Assessed consequence: **Small (1)**

Comment: As such no big consequences could be faced by nitrogen leakage still it's good to be on safer side by monitoring it.

Risk:

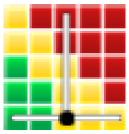


Consequence area: Materielle verdier

Assessed consequence: **Large (3)**

Comment: Nitrogen flowing with high pressure can cause problem and it should be done with great care. For this pressure monitoring is done continuously

Risk:



Incident: Pressure and temperature rise during experiment.

There is a possibility that temperature and pressure can go up during experiment. Temperature is controlled by external heater and pressure is also maintained during experiment. But they can go up during experiment.

Likelihood of the incident (common to all consequence areas): **Unlikely (1)**

Kommentar:

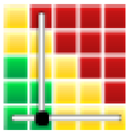
As the sensors installed on the reactors are monitoring the reading continuously. There is less possibility that it can go wrong.

Consequence area: Materielle verdier

Assessed consequence: **Medium (2)**

Comment: The pressure can damage the rig pipes if gets very high over the save limit and same goes with the temperature and can damage the rig. The filter can be damaged big time with pressure build up and temperature can affect the products yield as well and can heat up the reactors more then the safety limit.

Risk:



Incident: Glassware are fragile

Glass vials are fragile and can break if they get struck with each other very fast or if they fell on ground.

Likelihood of the incident (common to all consequence areas): **(0)**

Kommentar:

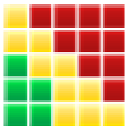
[Ingen registreringer]

Consequence area: Materielle verdier

Assessed consequence: **()**

Comment: [Ingen registreringer]

Risk:



Hazard: Rotary Evaporator usage

Incident: Cooling water leakage.

Cooling water can be leaked from pipes connecting at different points.

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

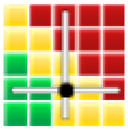
Before using the equipment, cooling water is flowed in the condenser and to check whether is there any leak or not.

Consequence area: Materielle verdier

Assessed consequence: **Large (3)**

Comment: Water can cause electrical failure and or cause problems to run the equipment safely.

Risk:



Incident: Acetone spillage.

Acetone can be spilled up while removing flask if vacuum is still present.

Likelihood of the incident (common to all consequence areas): **Unlikely (1)**

Kommentar:

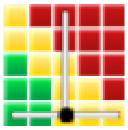
It is done with great care and vacuum is removed before separating out the flask.

Consequence area: Helse

Assessed consequence: **Large (3)**

Comment: Acetone is dangerous if inhaled in large quantity.

Risk:

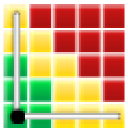


Consequence area: Ytre miljø

Assessed consequence: **Small (1)**

Comment: It can be problematic for the environment also but it evaporates quickly.

Risk:



Overview of risk mitiating measures which have been decided:

Below is an overview of risk mitigating measures, which are intended to contribute towards minimizing the likelihood and/or consequence of incidents:

Overview of risk mitigating measures which have been decided, with description:

Detailed view of assessed risk for each hazard/incident before and after mitigating measures

NTNU

Norwegian University of
Science and Technology