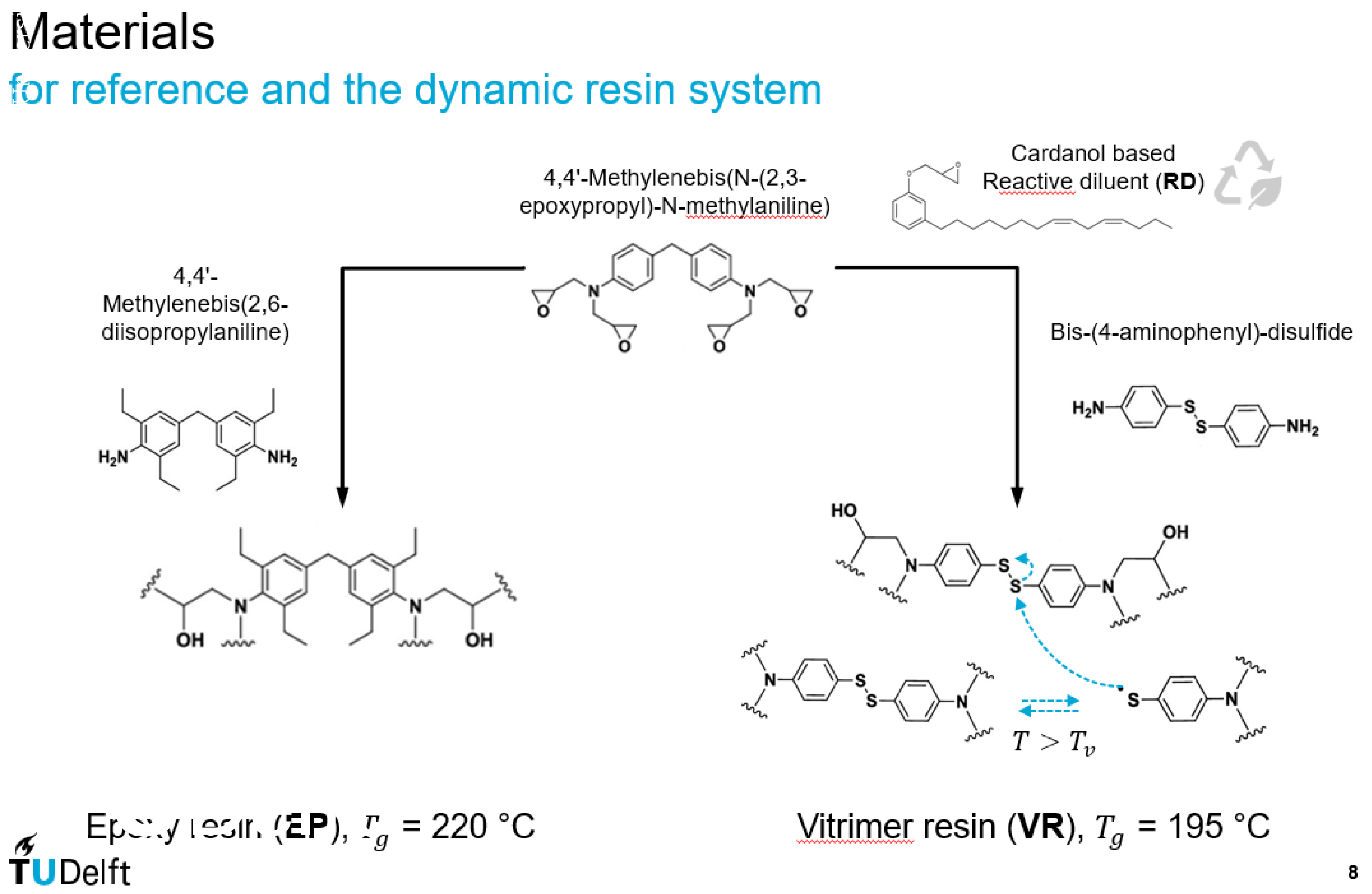
Recycling of Vitrimer Resins and Composites

Recycling of Vitrimer Resins and Composites using sub-critical Hydrothermal Liquefaction

CH3930: MEP

Vishal Venkatarangan



Materials

for reference and the dynamic resin system

4,4'-Methylenebis(N-(2,3-epoxypropyl)-N-methylaniline)

Cardanol based Reactive diluent (**RD**)

4,4'-Methylenebis(2,6-diisopropylaniline)

Bis-(4-aminophenyl)-disulfide

Epoxy resin (**EP**), T_g = 220 °C

Vitrimer resin (**VR**), T_g = 195 °C

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by

Vishal Venkatarangan

to obtain the degree of Master of Science at the Delft University of Technology,

to be defended publicly on Friday, September 26, 2025 at 3:30 PM.

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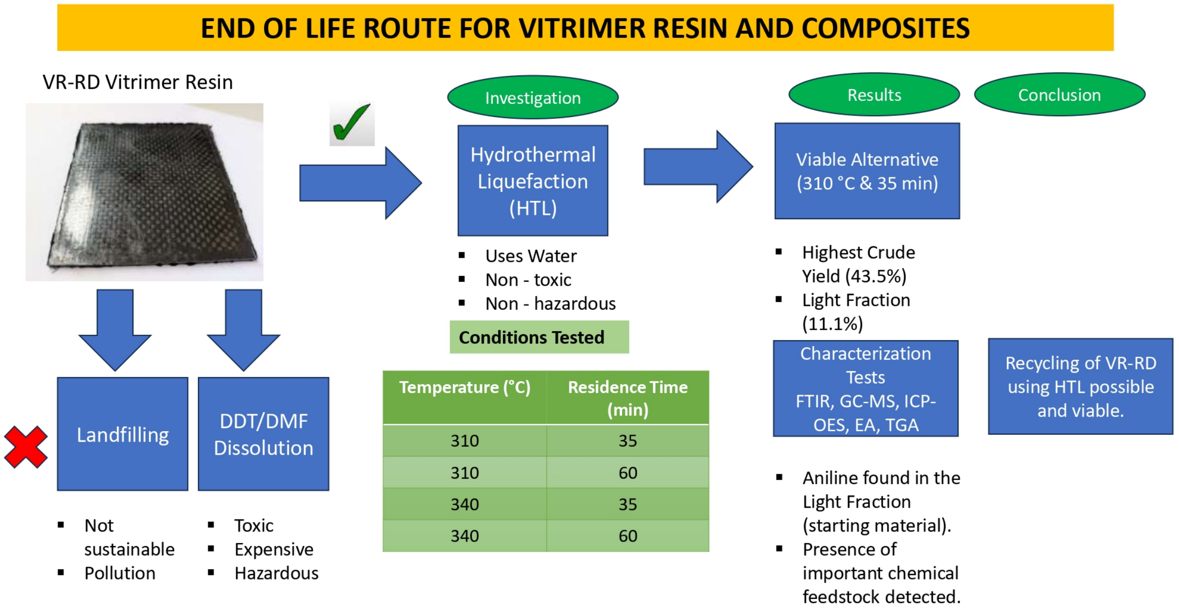
Thesis Committee Member:	Prof. Atsushi Urakawa
Project Duration:	January, 2025 - September, 2025
Faculty:	Faculty of Mechanical Engineering, TU Delft, Delft

Cover: Vitrimer Resin Structure
Style: TU Delft Report Style, with modifications by Daan Zwaneveld

TU Delft

Abstract



END OF LIFE ROUTE FOR VITRIMER RESIN AND COMPOSITES

VR-RD Vitrimer Resin

✓

Investigation

Hydrothermal Liquefaction (HTL)

- Uses Water
- Non - toxic
- Non - hazardous

Conditions Tested

Temperature (°C)	Residence Time (min)
310	35
310	60
340	35
340	60

✗ Landfilling

- Not sustainable
- Pollution

DDT/DMF Dissolution

- Toxic
- Expensive
- Hazardous

Results

Viable Alternative (310 °C & 35 min)

- Highest Crude Yield (43.5%)
- Light Fraction (11.1%)

Characterization Tests
FTIR, GC-MS, ICP-OES, EA, TGA

- Aniline found in the Light Fraction (starting material).
- Presence of important chemical feedstock detected.

Conclusion

Recycling of VR-RD using HTL possible and viable.

Figure 1: Abstract

Acknowledgements

This thesis was made possible through the support, encouragement, and kindness of many individuals, whose contributions rendered the journey not only successful but also meaningful.

Sustained guidance and thoughtful feedback were provided by the supervisors, Professor Dr. L.L. (Luis) Cutz IJchajchal, Professor Dr. B. (Baris) Kumru, and Dr.ing. N. (Niklas) Lorenz. They also provided positive encouragement when setbacks arose and shared light-hearted moments over lunch, coffee, and after work. This made working in the project truly enjoyable and filled with learning. This also provided encouragement to work harder in the project. Sincere thanks is also extended to Prof. Atsushi Urakawa for agreeing to be part of the thesis defence committee.

Support staff such as Michel and Neeha provided invaluable assistance. They imparted initial practical laboratory knowledge and skills which were essential before performing experiments. They also guided on how to perform the post experimentation analyses. Hence, their contribution is profoundly acknowledged and admired.

Special appreciation is extended to The Waterlab at TU Delft Faculty Of Civil Engineering and Geosciences for offering their reactor when the main reactor was in repair. They also assisted with the setting up of the new reactor and information on how to operate it.

Heartfelt gratitude is expressed towards all the various researchers and research groups which performed the characterization tests on the products obtained during the experiment. Gratitude is also extended to the researchers who helped with performing the characterization tests. This help proved to be crucial for this project and forms a majority of the results presented and discussed.

Lastly, warmest thanks are due to all of my friends and family. Their unwavering belief and support, even from afar, formed the foundation for every step that was taken.This project has been challenging, rewarding, and deeply fulfilling. Beyond engineering, lessons in patience and persistence were learned, and a lasting awareness was gained of how fortunate it is to be surrounded by people who care.

Generative AI (ChatGPT 5) and Grammarly have been only used for sentence formation, correcting grammatical inaccuracies, and generating code for LaTeX.

Vishal Venkatarangan
Delft, September 2025

Contents

Nomenclature

Abbreviations

Abbreviation	Definition
ISA	International Standard Atmosphere
BPA	Bisphenol A
ECH	Epichlorohyrin
CAN	Covalent Adaptive Networks
DTT	Dithiothreitol
DMF	Dimethylformamide
HTL	Hydrothermal Liquefaction
MEP	Master's End Project
EU	European Union
4-AFD	4-aminophenyl disulfide
DGEBA	Glycidyl Ether Resin
2-AFD	2,2′-Diaminodiphenyl disulfide
DDM	4,4′-Methylenedianiline
BGPDS	Bis(4-hydroxyphenyl) disulfide
WFW	Wet Filament Winding
PP	Polypropylene
PE	Polyethylene
HIPS	High-Impact Polystyrene
TA	Terephthalic acid
PET	Polyethylene Terephthalate
PC	Polycarbonate
PVC	Poly-vinyl chloride
CH	Char
HF	Heavy Fraction
LF	Light Fraction
IF	Intermediate Fraction
AP	Aqueous Product
NMR	Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
GC-MS	Gas Chromatography–Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
TGA	Thermogravimetric Analysis
FT-IR	Fourier Transform Infrared Spectroscopy
EP 600	EPOKITE 600
MAWL	Maximum Allowable Water Loading
ppw	parts per weight
rpm	rotations per minute
DCM	Dichloromethane

Abbreviation	Definition
ATR	Average True Range
RSM	Response Surface Methodology
TEA	Techno-Economic Assessment
LCA	Life Cycle Analysis
DoE	Design of Experiments
PTFE	Polytetrafluoroethylene

Symbols

Symbol	Definition	Unit
m	mass	[kg]

1

Introduction and Problem Definition

1.1. Introduction

Epoxy resins are thermosetting polymers that contain reactive epoxide groups. They are formed by reacting compounds such as Bisphenol A (BPA) with other compounds such as Epichlorohydrin (ECH) and then curing them with compounds known as hardeners [1]. They are used in numerous applications. These applications include adhesives, cement and mortar binders, coatings, rigid foams, and as a base for fibre-reinforced plastics and for electrical devices (potting resins). Their wide application and uses are possible due to their superior characteristics, such as good thermal stability, high mechanical strength, etc. The aerospace industry is one of the important industries where epoxy resins are used [2]. Often, epoxy resins act as the base for the fiber. Carbon or glass fibres usually constitute the primary material which are embedded in the resin. Epoxy resins are made up of complex three-dimensional cross-linked molecular structures, and thus, they are often very difficult to recycle. Hence, about 40-70% are disposed of in landfills (end-of-life) or pyrolysed [3]. The former is not a long-term sustainable solution, and the latter is energy-intensive and not environmentally friendly. Therefore, in the 2010s, a novel resin was synthesized, which proved to have better recyclable properties. They are called Vitrimer resins [4].

Vitrimer resins are similar to epoxy resins. However, they contain an additional feature. This feature is called dynamic cross-linking bonds. The formation of dynamic cross-linking bonds is achieved by integrating Covalent Adaptive Networks (CAN) into epoxy resins. Vitrimer resins not only promised enhanced thermoset properties but also assured recyclability, malleability, and self-healing characteristics. This is because CANs are reversible in nature. This makes them recyclable even after being cured, unlike epoxy resins [5]. Lorenz et.al prove the possibility of mechanical recycling of vitrimer resins [4]. Currently, vitrimer resins are predominantly recycled by mechanically comminuting the used resin pieces and reconsolidating them at about 200°C to form a resin material similar to the virgin one. However, the recycled vitrimer resin showed reduced thermal stability and even some degradation during the recycling process. This suggests that after a certain number of recycling steps, the material would have degraded and lost its mechanical properties beyond the usable limit, and hence would have to be discarded. This indicates that Vitrimer Resins cannot be mechanically recycled for more than a certain number of times. Hence, it is imperative to develop a process where recycling of vitrimer resins would be possible chemically, a process where chemical degradation of the material leads to substantial recovery of the base chemicals, which can be reused to make virgin vitrimer resins or for other applications. There has been some preliminary research on the chemical recycling of vitrimer resins using Dithiotheritol (DTT) and Dimethylformamide (DMF) solutions. This has been further discussed in section 2.1. Another innovative process, to recycle vitrimer resins and composites, is Hydrothermal Liquefaction (HTL).

HTL is a thermochemical process that employs water to break down substances chemically. The popularity of HTL is on the rise from 2009 onwards, as seen in Figure 1.1 [6]. This is because HTL is

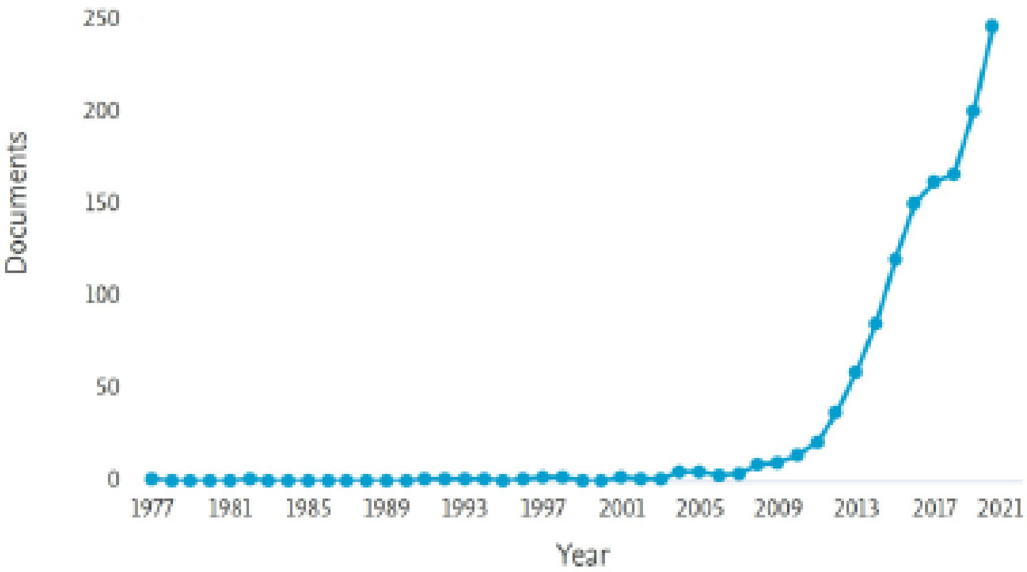


Figure 1.1: Hydrothermal Liquefaction documents by year. Figure reproduced from Esteban et.al.

truly an efficient recycling method with many advantages. The temperature and pressure of water are raised to about 374°C and 220.64 bar (water's critical point). At these temperatures, water acts as a powerful organic solvent and breaks down many known materials. HTL performed at temperatures and pressures lower than the critical point is called sub-critical HTL, and HTL performed at temperatures and pressures higher than this is called super-critical HTL. Owing to its generally low processing temperature and high energy efficiency, HTL is considered a viable technology for investigation in this project. Other advantages of HTL are: no processing required for feedstock, milder conditions than other processes, such as pyrolysis, and production of high-energy crude oil. Until recently, several publications have been issued that prove the capability of the HTL process to successfully recycle various types of biomass [7] [6] [8]. However, in this study, HTL is used to recycle Vitrimer Resin, which is of a non-biogenic source. This is not new but quite rare, according to the literature review. However, due to the enhanced properties of water at such conditions, it is hypothesized that HTL will be effective for polymers of non-biogenic origins as well.

The aim of this Master's End Project (MEP) thesis is to develop a novel process to recycle vitrimer resins to retrieve their base chemicals thermochemically. Landfilling of vitrimer resins is prevented through a process in which, rather than merely extending service life via mechanical recycling, the resins are chemically recycled by hydrothermal liquefaction, thereby enabling full material renewal.

1.2. Problem Statement

Based on the literature review conducted, the author believes that no processes have been developed to recycle vitrimer resins thermochemically (using HTL) to date. This is because research on vitrimer resins is limited compared to that on epoxy resins. They are yet to replace epoxy resins on an industrial scale. Currently, annual vitrimer resin production is about 0.25% to 0.65% of annual epoxy resin production [9] [10]. Apart from a couple of European Union (EU) funded research projects, only two companies are actively involved in vitrimer resin production-ATSP Innovation and Mallinda [11]. This significantly limits the recycling of vitrimer resins, as more attention is given to the recycling of epoxy resins. It is also challenging to establish a chemical recycling procedure for vitrimer resins, as the chemistry of recycling vitrimer resins remains unknown, and only a few reaction mechanisms have been proposed. These mechanisms will depend on the type of process used for the recycling. However, when suitable applications are found for vitrimer resins and their production increases, the problem of large-scale landfilling of them also becomes apparent. Hence, to resolve this, a chemical recycling method for vitrimer resins and then vitrimer composites (resin + fiber material) needs to be developed. This process has to be technically and economically feasible as well.

1.3. Research Questions

The following research questions are considered for this MEP project.

1. Can subcritical HTL chemically break down or degrade vitrimer resin or composite?
2. Under what experimental conditions will the hydrothermal liquefaction of vitrimer resin and composite be possible?
3. Which experimental condition produce the highest yield of favorable products?

2

Literature Review

2.1. Vitrimer Resin and Composite

Dynamic covalent bonds or dynamic crosslinks are the vital component of vitrimer resins. They are reversible covalent linkages that enable chemical adaptability to an externally applied stimulus. They exhibit their dynamism through one of two studied mechanisms. They are the associative bond exchange mechanism and the dissociative bond exchange mechanism. In the associative bond exchange mechanism, the bonds are broken along with the formation of new bonds. This leads to a rearrangement of the network without any depolymerization. Overall, crosslinking density is maintained. In the dissociative bond exchange mechanism, the bonds are temporarily broken and reformed. This leads to a brief reduction in the overall crosslinking density. Many types of associative bonds exhibit such dynamism. Some of them are: disulfide methanesis, transesterification, and imine exchange, etc. [12].

The presence of dynamic covalent bonds leads to the formation of covalent adaptive networks(CANs) (shown in Figure 2.1). The presence of such bonds in these networks provides a macroscopic flow to the material. Dynamic covalent bonds rearrange in response to external stimuli, such as thermal or light (photonic) energy. The presence of CANs in a material makes it reusable, reprocessable, recyclable, and susceptible to post-polymerization manipulation. For example, in crosslinked materials composed of thermoreversible covalent networks, applying high temperatures and pressure can cause molecular rearrangement without reversible degradation. This allows the material to be reprocessable, unlike traditional thermoset epoxy resins [12] [13]. The resins containing such CANs are known as vitrimer resins, and their thermochemical recycling is the main focus of this study. Further details of the resin analyzed are provided in the following paragraph.

The particular vitrimer resin analyzed in this study is 'VR-RD' made using 4,4′-methylenebis[N, N-bis(2,3-epoxypropyl)aniline], 4-aminophenyl disulfide (4-AFD) (curing agent), and a reactive diluent (LITE 513DF). The synthesis procedure is further explained in section 3.1. The dynamic covalent bonds present in our material are the aromatic disulfide bonds present in 4-AFD. They rearrange according to the associative bond exchange mechanism. The epoxy groups of the resin react with the amine groups of the 4-AFD to form thermoreversible covalent cross-linked networks. The newly synthesized VR-RD's mechanical properties have been compared to those of a two-component aero-grade qualified epoxy resin. Properties such as elastic modulus (stiffness), flexural properties, compression behaviour, and creep resistance were compared. VR-RD exhibited a more noticeable decline in stiffness and better creep resistance, while being similar in the other properties, compared to the two-component aero-grade qualified epoxy resin. The mechanical recycling of VR-RD was also tested. VR-RD was comminuted and reconsolidated using a hot press at about 200°C and 20 MPa for 0.5 hours. This recycled VR-RD was found to have similar mechanical properties to the virgin VR-RD, except for some loss in mechanical strength (glass transition temperature reduced by 4°C). VR-RD also showed good reformability at 200°C, unlike the two-component aero-grade qualified epoxy resin. The research does not mention how many times VR-RD can be mechanically recycled before the degradation in mechanical properties crosses the acceptable limit [4]. However, it is not sustainable to repeatedly mechanically

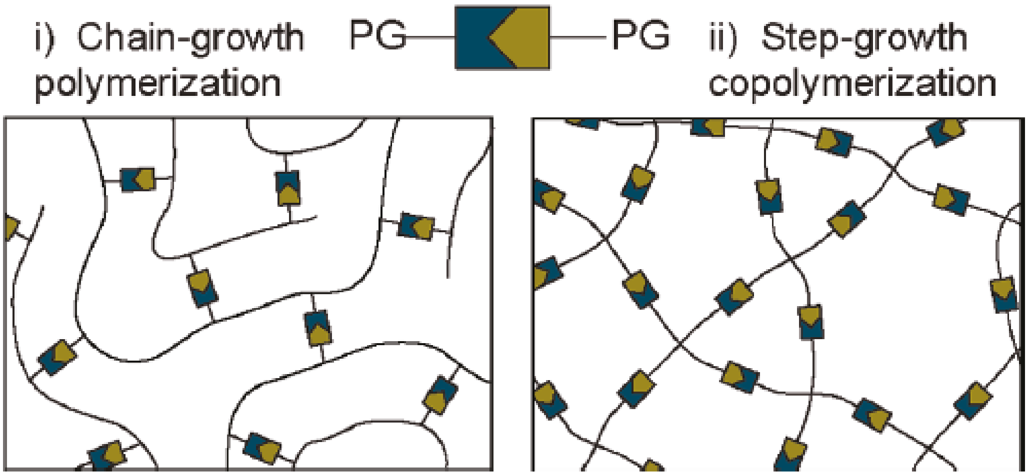


Figure 2.1: Covalent Adaptive Netowrks (CANs) . PG stands for Polymerizable Group. Figure reproduced from Kloxin et.al.

recycle vitrimer resins and then landfill them. It would be productive to utilize the better recyclability of vitrimer resins to chemically recycle them and efficiently retrieve the starting reagents and monomers.

Chemical recycling of VR-RD has not been tested. However, chemical degradation of other vitrimer resins has been tested. Liu et.al tested chemical degradation recycling on the vitrimer resin produced by them. This vitrimer resin was made using Bisphenol A glycidyl ether resin (DGEBA) (epoxy agent), 2,2'-Diaminodiphenyl disulfide (2-AFD) (curing agent), and 4,4 4,4'-Methylenedianiline (DDM). The resin samples were immersed in a 0.05 g/ml DTT/DMF solution at 90°C and observed hourly. DTT stands for dithiothreitol, and DMF stands for dimethylformamide. Complete degradation of the resin was observed after 2-4 hours of immersion. The resultant substances after the degradation process were an epoxy oligomer and the organic solvent DMF (degradation solution). This oligomer is devoid of disulfide covalent bonds (-S-S) and is composed of -SH sulfhydryl groups. There is a potential to re-create the disulfide covalent bonds by oxidizing them at high temperatures. However, this recovery step is not explored further. The mechanism of dissolution is theorized to be this: DTT enables thiol-disulfide exchange reactions and reduces the disulfide bonds from S-S to -SH. This is further enabled by DMF, which acts as a swelling agent and widens the intermolecular chain spacing. This paper further proposes that the degradation solution itself could be used as a curing agent to make new vitrimer resins [14].

Si et.al also researched the chemical degradation of their vitrimer resin. Their resin, a dual disulfide vitrimer resin, is made using Bis(4-hydroxyphenyl) disulfide (BGPDS) (epoxy agent) and 4-AFD (curing agent). Additionally, a single disulfide vitrimer resin, DGEBA, was also tested. Both resins were dissolved in a 0.1mg/ml DTT/DMF solution, and the residual weight of the resins was recorded over time. Both resins showcased good dissolution in the solvent. The dual disulfide vitrimer showed better dissolution than the single disulfide vitrimer. This is due to the higher presence of aromatic disulfide bonds and the better fragmentation of the molecules in the presence of thiols. The mechanism of dissolution is believed to be similar to what is theorized in Liu et.al [15].

Hence, these two papers conclude that the chemical recycling of vitrimer resins is possible. However, if these methods are scaled up, they rely on vast amounts of DMF, which is expensive and requires a special handling procedure as it is toxic. DTT is hazardous and is not easily scalable. This method is time-consuming and also not good at handling other materials, such as fillers [16] [17]. Hence, HTL presents itself as a viable recycling route that is devoid of these problems.

HTL employs water (which is not toxic and harsh to handle) to break down the substances. It is also easier to scale up. The temperatures and pressures are also not high compared to other thermochemical processes, such as pyrolysis. Therefore, HTL is a viable option to consider. The presence of hydrophilic polar groups and enhanced void space in vitrimer resins explains the increased moisture absorption rate compared to conventional epoxy resins [14]. This could prove beneficial while performing HTL on vitrimer resins, as water is the primary solvent.

Combining vitrimer resin with fibres such as carbon fibres for reinforcement results in vitrimer composites. Although vitrimer composites were not experimented with in this study, they were still covered in the literature review, as the successful recycling of the composites is the long-term goal of this project. The primary composite studied was carbon fiber reinforced VR-RD vitrimer resin. This was produced using the Wet Filament Winding (WFW) method. In this method, carbon fibres were impregnated into the resin. The composite was found to have enhanced mechanical properties such as tensile strength and storage modulus. Hence, it is found to be more suitable for application in industries such as the aerospace industry. Si et.al demonstrate the removal of the vitrimer resin from the carbon fibre by dissolving the composite in a solution of 0.1mg/ml DTT/DMF solution. This removes the resin in 1 hour producing bare carbon fibres. These recycled fibres were then impregnated into fresh resin to form recycled vitrimer composites which showcased similar mechanical properties to a virgin composite. The recovery of carbon fibres from the composites is thought to be important economically and for the composites life to be circular [18].

2.2. Hydrothermal Liquefaction

Sub-critical Hydrothermal Liquefaction (HTL) is the choice of recycling method used for this thesis study. In this kind of HTL, the water is subjected to conditions below it's critical point of 374°C and 220.64 bar. The reaction mechanism of HTL is first discussed followed by some factors which can affect the product yield and applications for the products produced.

2.2.1. Reaction Mechanism

The ability of water to act as both a reactant and a catalyst makes HTL a feasible recycling process for many materials. At sub-critical conditions, it is theorized that water acts as a reactant through the ionic reaction mechanism. The dissociation constant of water (Kw) is reported to be high in these conditions. At high temperatures, the increased thermal energy weakens the hydrogen-bonded network of water molecules [19]. This in turn enhances the dissociation of water into H^+ and OH^- ions. This makes it a highly reactive solvent that is capable of facilitating cleavage and other types of decomposition reactions. Less hydrogen bonding also leads to a decrease in properties such as viscosity and surface tension. This allows for greater diffusion of molecules and overall decrease in the orderly nature of the network [20] [21]. At sub-critical conditions, a remarkable decrease in the dielectric constant of water is noted (compared to ambient conditions). At 300°C and 100 bar pressure, water is found to have a dielectric constant similar to ethanol [22]. This allows for non-polar molecules to be dissolved as there is reduced polarity and reduced energy penalty to pay. This increases the solubility of non-polar organic molecules in water and decreases the solubility of polar molecules, which need electrostatic attraction for dissolution [23].

Three major steps that occur during HTL to the feed are depolymerization, decomposition, and recombination. During depolymerization, the complex molecules of the feed are broken into basic building blocks or monomers. Plastics with heteroatoms in their main chains exhibit decomposition into their monomers with good liquefaction efficiency. Plastics which lack heteroatoms, such as poly-olefins and aromatics, demonstrate sufficient cracking of their main chains and subsequent decomposition [24]. These monomers then undergo other reactions such as bond cleavage, retro-aldol reactions, rehydration, dehydration, isomerization, etc., during the decomposition step. Polyolefins were observed to decompose into saturated and unsaturated hydrocarbons through hydrogen abstraction and β-scission. Plastics like polystyrene, which are composed of weak benzylic C-C bonds, undergo cracking between the main chain and benzene. Polyvinyl Chloride is subjected to dechlorination through either dehydrochlorination or hydroxide nucleophilic substitution. Condensation polymers are expected to experience decarboxylation [24]. The decomposition of each material depends on the types of atoms and bonds present in it and can vary. Hence, when a feed material contains a multitude of components, it is difficult to determine the exact decomposition process. Post this step, these monomers repolymerise or recombine during the recombination step to form the final HTL products [20] [21]. For polyolefins, observed recombination products were cyclics and aromatics. In the case of polyvinyl chloride, dechlorination leads to the formation of solid products (char)[24].

As VR-RD is an epoxy-based polymer containing heteroatoms such as oxygen, nitrogen from amine hardeners, sulfur from disulfide bonds, and oxygen or nitrogen from the cardanol-based diluent, it is prone to depolymerization through hydrolysis in subcritical water. Under these conditions, water molecules attack and cleave ester, ether, or amide linkages within the polymer's backbone or crosslinked structure, thereby reducing the material into smaller fragments.

At reaction temperatures of 310–340 °C, which are well above the reported 5% mass loss temperature (285 °C) of VR-RD, significant thermal degradation is expected. Disulfide bonds, which provide the dynamic properties of the vitrimer, are particularly unstable at elevated temperatures. These bonds are known to degrade and cleave above 200 °C, with notable degradation already observed below 220 °C. Consequently, alongside the dynamic bond exchange process—which becomes active above the vitrimer's glass transition temperature —direct thermal cleavage of the disulfide linkages proceeds as a major degradation pathway.

The cardanol-based reactive diluent present in VR-RD plays an important role in lowering the glass transition temperature and broadening the reprocessing window, thus imparting increased plasticity and enabling processing at reduced temperatures. However, under the high-temperature conditions of 310–340 °C, the diluent itself undergoes degradation. Its decomposition typically follows a two-step pathway, with the aliphatic side chains beginning to degrade around 350 °C, which means that the diluent is also expected to contribute to the composition of the degradation products [18].

If amine-based hardeners such as 4-AFD are employed in the formulation, the nitrogen within the hardener can generate ammonia under hydrothermal conditions. This ammonia subsequently makes the water medium alkaline and acts as an in-situ catalyst, accelerating hydrolysis and depolymerization reactions within the system [25] [26].

The breakdown of epoxy-based materials in hydrothermal environments generally produces phenolic compounds. Studies on similar epoxy systems and polycarbonates have consistently shown the formation of BPA and a range of phenols, including phenol itself, cresols, and isopropylphenols, which are distributed between the aqueous and oil phases. Given the structural similarity of VR-RD, the appearance of analogous phenolic compounds is anticipated [25] [27].

The effect of reaction time is significant. At longer residence times, such as 60 minutes compared with 35 minutes, a greater degree of depolymerization is achieved owing to extended exposure to hydrothermal conditions. However, at higher temperatures, particularly around 340 °C, extended durations favor secondary reactions. These include further cracking of primary degradation products into smaller molecules, as well as dehydration, demethylation, and hydrogenation processes that yield more stable aromatic hydrocarbons such as toluene or ethylbenzene. At the same time, condensation reactions between fragments may produce larger, more complex structures. Prolonged exposure can also result in the formation of char or coke, as has been widely observed for other polymers under similar conditions. This char formation reduces the yield of desirable liquid products and negatively affects product purity.

In summary, hydrothermal liquefaction of VR-RD at 310–340 °C for 35–60 minutes proceeds through combined hydrolysis and thermal degradation of the epoxy matrix and disulfide bonds. Phenolic compounds are expected to dominate the product distribution, while higher temperatures and extended residence times promote secondary reactions and increase the risk of char. formation.

2.2.2. Factors affecting product yield

Since the majority of these studies are performed on biomass, the factors affecting the product yield of other materials when they are hydrothermally liquefied are theorized based on these studies.

Feed composition plays a major role in determining the product yield. For instance, the presence of lipids over other biomolecules, such as proteins and carbohydrates, can lead to increased biocrude yield. This is due to the varying thermal stability of the fatty acids produced from the different molecules [21] [28]. Heightened yields of biochar production are observed when the feed contains lignin. This is due to the possibility of reactive lignin intermediates crosslinking to repolymerize [21] [7]. The presence of ash and inorganic minerals is found to have an influence on the biocrude formation and product distribution. Presence of phosphorus may deter the formation of biocrude, while the presence of sodium may improve it [21] [28] [29]. However, due to the inconsistent chemical composition of biomass, it is very difficult to ascertain the dependence of product yield on feed composition.

Reaction parameters such as reaction temperature, residence time, pressure, heating rate, solvent type, and ratio affect the product yield the most. Reaction temperature is noted to be one of the most important parameters affecting product yield. It is observed that biocrude yield generally increases with an increase in temperature until an optimum point is reached. Post this optimum temperature, the yield decreases due to factors such as thermal decomposition and excessive cracking. The optimum temperature of liquefaction (or range of temperatures) is different for every type of biomass and is established through experimental study. Reduced hydrogen-donating capacity of water, increased repolymerization, and increased shift towards free-radical mechanism from ionic mechanism are the possible reasons for lower product yields at higher temperatures. The temperature also affects product quality by influencing the H/C ratio of the biocrude and the diversity of compounds present [21] [7] [30].

The influence of residence time on product yield is significant. The highest product yield can be expected when the HTL is performed for an optimum time range. This range is found by experimentation and differs from material to material. Prolonged residence times (above the optimal range) can lead to secondary reactions. These secondary reactions can subsequently lead to increased biochar and gas formation. Insufficient residence time could lead to improper cracking and thus increase char production and decrease reaction efficiency. It is noted that the concentration of nitrogen-containing compounds and phenolic compounds increases in the biocrude when the residence time is increased [7] [29].

Pressure plays a crucial role in maintaining the water and biocrude in the same phase and minimizing the formation of gaseous products. Pressure determines which reaction mechanism is more prevalent than the other. Higher pressure can lead to an increase in the alkene-to-alkane ratio and heavier hydrocarbons in the biocrude due to the quenching of radicals [24].

Generally, the faster the heating rate, the higher the yield of biocrude observed. However, the heating rate is fixed for a particular reactor system and is not treated as a factor to be experimented with.

Catalysts also impart a major influence on product yields. The general trends that have been noticed among various studies indicate that acidic catalysts tend to lower the biocrude yield, while basic and alkali catalysts tend to improve the biocrude yield. This is because alkali catalysts contribute towards the promotion of single-ring aromatic compounds and inhibit dehydration and repolymerization. Potassium salts such as K_2CO_3 and KOH exhibit higher catalytic activity. In terms of the phase of the catalyst, heterogeneous catalysts are generally preferred. This is due to the ease of separation they offer post the HTL process. However, heterogeneous catalysts could accumulate in the biochar and are not preferred in HTL, where the biochar is important. The effect of co-catalysts (a combination of homogeneous and heterogeneous catalysts) is also explored on the biocrude yield and quality [21] [8].

The solvent used for the reaction can also affect the product yield. Although water is the most commonly used solvent in HTL studies, research has also been conducted on using organic solvents (such as ethanol, isopropanol, and methanol) and hydrogen donor solvents [21].

The pH of the reaction medium can affect the production of biocrude. An acidic environment can reduce the biocrude yield, while alkaline conditions can increase it. Production of organic acids such as carboxylic acids can lower the pH and make the system more acidic [21] [24].

Lastly, other factors that have a minor influence over the product yield are reactor type and configuration. There could be a difference in the product yield if a continuous reactor system is used in place of a batch reactor, keeping other parameters constant. The presence of stirring could improve the yield by bettering the contact between the feed and water.

2.2.3. Application of the produced crude oil (and fractions)

The application of the produced crude oil or other products, such as char, depends on their chemical composition. This is determined by the chemical composition of the original material. The main objective is to convert waste materials into highly valuable fuels and energy sources. The conversion of polyolefin wastes such as polypropylene (PP) and polyethylene (PE) into profitable oils and fuels is observed by [31]. Colnik et.al converted PE wastes, under supercritical conditions, to hydrocarbons of C6-C8 chains (gasoline fraction) and C9-C20 chains (diesel fraction). These products can be further processed to form fuels for heating and energy purposes [32]. Bai et.al observed the production of toluene and ethylbenzene after the hydrothermal depolymerization (under supercritical conditions) of High-Impact Polystyrene (HIPS) along with styrene monomer [33]. Ethylbenzene and toluene are two important chemical reagents that have a multitude of applications in the industry. Ethylbenzene is used in the production of styrene and other synthetic polymers. It is also used as a solvent [34]. Toluene, depending on the grade, is used as an industrial organic solvent and precursor to many commercial goods [35]. The production of various crude oils from biomass and polymers using sub-critical hydrothermal liquefaction was analyzed by Souza et.al [25]. Some common compounds that were synthesized were p-isopropenyl phenol, Benzoic acid hydrazide, toluene, and cyclopentanone. All of these compounds have industrial applications. A linear trimer of p-isopropenyl phenol has the potential to be used as a precursor for epoxy resin production as a curing agent [36]. This, along with styrene production from ethylbenzene, helps in making the life of polymers circular. Apart from crude oil, in some experiments, the solid products were also determined to be important. During the HTL of Polyethylene Terephthalate (PET), the monomer, terephthalic acid (TA), was obtained as the solid product. This helps in making the value chain of PET polymers circular. Souza et. al also report the recovery of monomers from the HTL of many polymers. This includes recovery of BPA, phenol, and p-isopropyl phenol from the HTL of Polycarbonate (PC). This also includes the recovery of Caprolactam from the HTL of Polyamides and the above-mentioned TA from the HTL of PET. This helps in making the value chain of these polymers circular [25]. Laredo et.al observed that post-HTL PC char has increased energy density compared to PC and could be used as a solid fuel for heating and energy generation purposes. One of the studies reviewed by Georgina et. al identified that dechlorinated solid residues from the HTL of Poly-vinyl chloride (PVC) could act as a source of carbon [27]. Mattsson et. al report studies where a high calorific oil (40 MJ/kg) was obtained from the solvolysis of glass fibre-reinforced polymers. This oil could potentially have applications in heating and energy generation. The oil was sourced mainly from the resin and glass fibres, which were recovered, and had about 70-75% of the original mechanical strength and can be reused for applications demanding lower mechanical strength [37]. Ferjan et. al report the use of solvolysis to chemically recycle multi-material and multi-layer plastics. In this case, the resin is recovered as a monomer or oligomer, which can be used as a chemical feedstock. The recovered fibres are not mechanically strong enough to replace virgin fibres. However, they can be converted into new thermoplastic composites, moulding compounds, and non-woven fibre fabrics. They can also be reused as reinforcement or filler in new composite structures and other applications. This is not ideal and doesn't make the value chain circular, but it contributes towards less landfilling of old fibres and less demand for virgin fibres. The study also reports that recovered glass fibres from polyester wind blades retain 80% of original fibre strength [38]. Zhang et.al report on the use of recovered carbon fibres in the production of sheet molded compounds for automotive parts manufacturing. The study also reports chemically recycling carbon fibres for 3-4 cycles, with each recycled product fit for an application with less stringent mechanical strength requirements than the other. This paper also suggests the use of recovered carbon fibres in applications such as thermoelectric materials, flexible batteries, heat insulation/sinks, and lithium-ion batteries [39].

This proves that products which would be obtained from the HTL of Vitrimer resins and composites have great potential to be used as A. monomors/oligomers to recreate the resin B. to convert them into fuel or chemical feedstock. This further strengthens the business case for performing HTL on Vitrimer resins and composites.

2.3. Characterization Testing

The Unicube Elemental Analyzer manual and Kandioller et.al were referred for Elemental Analysis. The Unicube Elemental Analyzer manual describes the method to prepare the sample, operate the machine, and perform the analysis. It also describes how to interpret the data given by the machine and how to deduce the Carbon%, Hydrogen%, Nitrogen %, Sulphur% (C, H, N, S %) composition values in the sample. Kandioller et.al describe the theory behind elemental analysis and how to carefully interpret the data and avoid errors. It outlines the importance of Elemental Analysis compared to other techniques such as Nuclear Magnetic Resonance (NMR) and High Performance Liquid Chromatography (HPLC). It also outlines how important elemental analysis is for the determination of primary substance characterization. The following suggestions were listed to keep the deviation in the results of each sample to a maximum of 0.05%. They are: 1. Keep the instruments the same 2. monitor the range of the weighted sample amounts and accuracy of weighing, 3. account for the limit of quantification for each element, 4. ensure that the reference material (used for calibration) covers the elemental % range of the measured samples, 5. the presented values are an average of multiple runs of the analysis [40] [41].

No particular literature was studied for Gas Chromatography-Mass Spectrometry (GC-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). This is because these tests were conducted by technicians at the P&E Chemical lab and other external labs. The final results were provided and presented in this study, and also analyzed.

Thermogravimetric Analysis (TGA) was primarily used to find the degree of cure, maximum degradation temperature, and glass transition temperature in these studies. They were also used to determine the thermal stability of the fully cured resin. The heating procedure and TGA methodology performed in this study were followed from Lorenz et.al and are explained in section 3.6.4. The cited papers were studied for performing TGA. [18] [14] [15] [4] [11] [42].

Papers Wang et.al, Mecozzi et.al, Lu et.al, and Nandiyanto et.al were studied for correct peak identification and determination of compounds from the obtained spectroscopy results of Fourier Transform Infrared Spectroscopy (FT-IR). Especially the procedure mentioned in Nandiyanto et.al to identify the compounds was followed, as the other studies focused on oils produced from biogenic sources and might not be relevant to the material studied. The procedure is as follows:

- Identify the overall FT-IR peaks.
- Check the single-bond region of 2500–4000 cm^{-1} (zone 1) and compare with the reference database.
- Identify the peaks in the triple-bond region of 2000–2500 cm^{-1} (zone 2) and verify with the reference database.
- Repeat this step for 1500–2500 cm^{-1} (zone 3, double-bond region) and for $< 1500\ \mathrm{cm}^{-1}$ (zone 4).

Following this procedure is sufficient for the identification of all the organic compounds and functional groups present in your sample [43] [44] [45] [46].

3

Materials and methods

3.1. Materials

The vitrimer resin (VR-RD) is made of three parts. 4,4’ -methylenebis[N,N-bis(2,3-epoxypropyl)aniline], LITE 513DF, and 4-aminophenyl disulfide (4-AFD). The parts per weight (ppw) of the components in the resin are 70, 30, and 63, respectively. 4,4’ -methylenebis[N, N-bis(2,3-epoxypropyl)aniline] constitutes part A of EPIKOTE 600 (EP 600). EP 600 is a two-component aero-grade qualified epoxy resin manufactured and sold by Westlake Corp. LITE 513DF is a multifunctional biobased cardanol-derived reactive diluent purchased from Cardolite Corp. 4-AFD is a chemical reagent purchased from Molekula Ltd [4].

The 4,4’-methylenebis [N, N-bis(2,3-epoxypropyl)aniline] is degassed at 300 mbar pressure. The VR-RD is then synthesized by mixing the degassed 4,4’-methylenebis [N,N-bis(2,3-epoxypropyl)aniline], 4-AFD, and LITE 513DF while providing sufficient heating to melt the 4-AFD properly. The resin is then cured to form the final product. The cured resin was comminuted to a particle diameter of less than 2 µm and used for the experiments.

The composite was synthesized using the following procedure: Dry carbon-weave fabrics (sourced from Suter Kunststoffe AG in Switzerland) were stacked in a symmetrical layup. The premixed VR-RD was poured into the open mould under a vacuum of 20 mbar. The laminate was heated at 2 $\mathrm{K \cdot min^{-1}}$ to 180 °C under a consolidation force of 2 kN, followed by an isothermal dwell at 180 °C for two hours under a consolidation force of 50 kN, by which the resin system was cured. The manufactured laminates exhibited in-plane dimensions of 80 × 85 $\mathrm{mm^2}$ and a thickness of approximately 1 mm.

3.2. Hydrothermal Liquefaction Process

The HTL process requires water (the primary solvent used) to be heated to high temperatures and elevated pressures (around 374°C and 220 bar). At these high temperatures and pressures, water acts as a powerful solvent that breaks down many organic and inorganic substances [8]. Two reactors were used to conduct the HTL experiments. The first reactor is a 4560 Mini Bench Top autoclave reactor with a movable vessel configuration. This reactor has been manufactured by Parr Instrument Company, United States of America. The volume of the reactor is 300mL and is fitted with a Polytetrafluoroethylene (PTFE) gasket to achieve a maximum operating temperature of 350°C. The reactors were then loaded with the sample (vitrimer resin) and with water. The reactors were loaded with reactants according to their respective Maximum Allowable Water Loading (MAWL) [47]. The MAWL for the reactor was calculated according to the following formula:

$$\text{MAWL} = \frac{0.9 \qquad (\text{Vessel Volume})}{\text{Volume Multiplier at Max. Temp.}} \tag{3.1}$$

The volume multiplier for experiments at 310°C is 1.5 and for 340°C is 1.73. This provides a maximum water loading of 180mL and 156mL for the 300mL reactor at 310°C and 340°C, respectively [47].

Once the reactor was loaded with the sample, it was attached to a magnetic drive A1120HC6 with high-pressure-rated metallic semi-circle clamps. These clamps were bolted to ensure the containment of pressure during high-pressure operations. The stirrer was attached to the stirrer motor, which had a 1/8 hp variable speed. The stirring was set to a constant 150 rotations per minute (rpm) for all experiments. 150 rpm was chosen as it provided enough circulation without overloading the stirrer motor. The atmosphere present in the reactor was purged and filled with nitrogen to maintain an inert environment. Once the purging had been completed, the heating jacket was fixed surrounding the reactor. The target setpoint of 310°C or 340°C was set in the Parr 4848 controller, and the heating was started. After the target temperature was reached and the experiment had been conducted for a residence time of 35 or 60 minutes, the heating was switched off and the heating jacket was removed. The reactor was allowed to air-cool till 250°C. Post this, it was cooled using hot water from 250°C to 100°C and then with cold water from 100°C to ambient temperature. The reason for choosing 340°C and 310°C for temperature and 35 and 60 minutes for residence time has been explained in section 4.1 [48].

3.3. Experimental Conditions

The experimental conditions that were varied were temperature and residence time. The temperature levels were set at 340°C and 310°C and the residence time were set at 60 and 35 minutes. Across all experiments, the sample-to-water (solid-to-solvent) loading was maintained at 1:17 (w/w). This procedure was followed from Souza et.al [25].

3.4. Product Separation

The summary of the Product Separation and enrichment procedure is provided in figure 3.1 below:

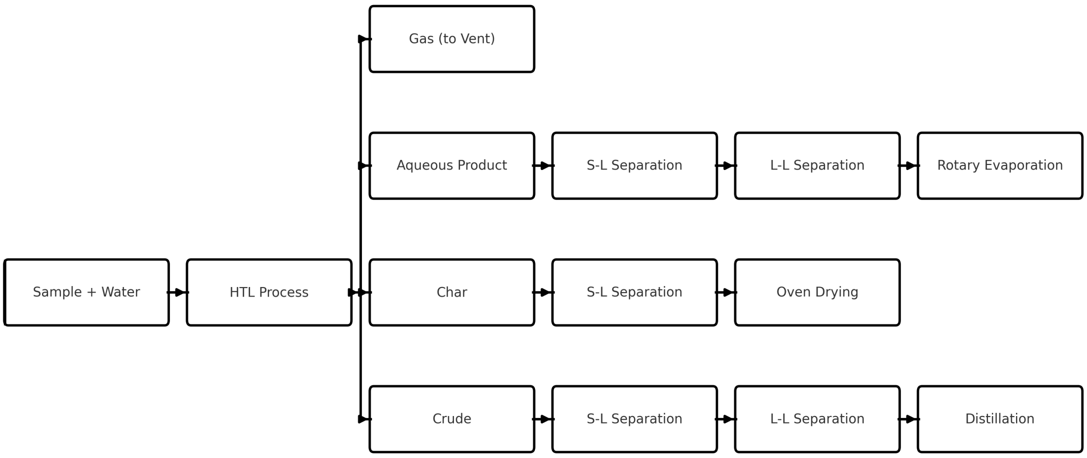


Figure 3.1: Product Separation flow diagram

The four main products obtained after an HTL are: 1. Gas, 2. Aqueous Phase, 3. Oil(Crude) and 4. Char. The products before enrichment are shown in figure 3.2.

The Gaseous phase is not recoverable as it is ventilated out via the fumehood once the reactor is depressurized and opened. Hence, it is not recovered and only its mass is calculated while doing the product distribution calculation. The calculation approach is detailed in the next section.

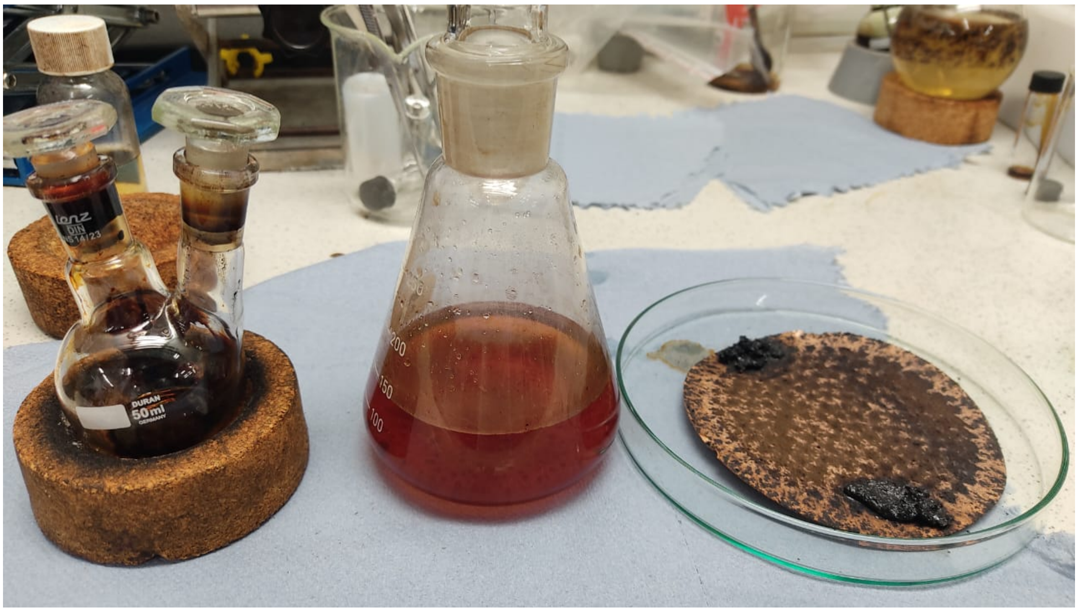


Figure 3.2: Products before enrichment (Left to Right: Crude, Aqueous Phase, Char)

The reaction mixture, which consists of the aqueous phase, oil, and char, is where the bulk of the product separation is performed. The stirrer blades and the thermocouple rod are scraped of any remaining solids or liquids to ensure minimal mass transfer losses. They are also rinsed with Dichloromethane (DCM). The liquid phase is transferred to a pre-weighed 250mL beaker and will be addressed as 'phase-1'. The solids are transferred to another pre-weighed 250mL beaker. Approximately 40mL DCM is used to rinse the reactor to transfer all the remaining solids and organic matter completely. This is done in 8 rinsing steps of 5mL DCM each. This rinsed DCM is transferred to the beaker containing the solids and will be called 'phase-2'.

Next, the solids are separated from the liquid mixtures. This step is called Solid-Liquid separation (S-L Separation). A grade 5 Whatman 2.5µm pore size filter paper is used for this purpose. Two Buchner flasks of 250mL each were pre-weighed and labelled Filtrate-1 and Filtrate-2. Phase 1 is first vacuum filtered in the Buchner flask labeled Filtrate 1 using filter paper. The solids are recovered on top of the filter paper. The process is repeated if the filtered solution still contains a significant amount of solids. This is determined by physical observation of solid particles in the flask labelled Filtrate 1. If a large amount of solid particles is observed in the flask, it can be inferred that a large portion of the solid particles have bypassed the filter paper, and the process needs to be repeated. After this has been done, phase 2 is vacuum filtered using the same filter paper but in another Buchner flask labelled Filtrate 2. The process is repeated if the filtered solution still contains a significant amount of solids. Rinsing of the beaker, which contained phase-2, is done twice using 5mL DCM each time. This rinsed DCM is poured over the same filter paper (and hence over the filter cake), and additionally, another 5mL DCM is poured over the filter cake to ensure complete extraction. This filter cake, or the solid particles retained by the filter paper, is the separated solid from the reaction products. It is dried at 105°C for 24 hours to remove as much moisture as possible. This dried filter cake is then weighed, and the mass is noted as m_{char}.

The solid-free Filtrate-1 and Filtrate-2 are then mixed together into a separatory funnel (500mL) and shaken well to ensure a good mixture between both liquids. The separatory funnel is then allowed to rest for some time for the two immiscible phases to separate. Filtrate 2, which mostly consists of organic substances, settles in the bottom layer, while Filtrate 1 makes up the top layer. Filtrate 2 is carefully separated and stored in a pre-weighed 250mL round-bottom flask. 5mL of DCM is then added to the remaining Filtrate 1 to extract the remaining organic substances, and the separatory funnel is shaken well for a good mixture. The funnel is then again allowed to rest for 5 minutes to obtain good phase separation, and the remaining organic substances are dissolved in the DCM and separated from Filtrate 1. The leftover Filtrate 2 is then transferred to another pre-weighed 250 mL round-bottom flask. This separation step is known as liquid-liquid separation (L-L separation).

Filtrate 2 is then attached to a rotary evaporator machine (mention exact machine name and model) to evaporate all the water. The round-bottom flask is attached to it using metallic clamps. The machine is then set at 40 rotations per minute (rpm), and the temperature of the water bath is set to 60°C. 60°C is chosen as the temperature is not hot enough to evaporate important compounds in the product. The temperature is also not high enough to degrade the product formed. The rotations ensure a uniform temperature distribution and consistent evaporation of water. The internal pressure is slowly reduced from ambient pressure to about 97 mbar. The machine is allowed to operate for a couple of hours until Filtrate 2 is devoid of any moisture content. This is known as the aqueous phase and is weighed, and the mass is noted as m_{aqueous}. The composition of it is analyzed. These steps are detailed in the future sections. The water, which is evaporated from the aqueous phase, is cooled down using a condenser column and collected in another round-bottom flask. This water is later discarded.

The Filtrate-1 collected from the separatory funnel is subjected to a two-step distillation process. In the first step, the distillation is first performed at a low temperature setting. This entails heating the reaction medium to about 100°C. This produces fumes at about 40°C. These temperatures are measured by thermocouples. This step is done to remove all the DCM used in the previous extraction processes. The DCM vapours are cooled using a condensation column and collected in a beaker. Once the temperature reading of the thermocouple measuring the temperature of the fumes starts dropping and the collection of liquid DCM in the beaker stops, the distillation is stopped momentarily. The remaining Filtrate 1 is known as the crude oil. This mass is noted as m_{crude}. This consists of light, intermediate, and heavy fractions. A small amount of this crude is weighed and stored separately to do composition analysis on it.

Once this has been done, the second step of the distillation process is started. The heating is switched on again, and the distillation is performed at a high setting. The reaction medium is heated to about 350°C, and the temperature of the fumes reaches about 120°C. These fumes are then condensed using a condensation column and collected in a small pre-weighed round-bottom flask. This collected liquid is known as the light fraction of the crude. The heating is continued until the collection of the light fraction stops in the small round-bottom flask, and the reading of the thermocouple measuring the temperature of the fumes starts decreasing. The contents remaining in the reaction mixture are known as the heavy fraction. The remainder of the crude, which might have been lost in the distillation equipment or columns and is not recoverable, is known as the intermediate fraction. The weight of these fractions and their compositions are analyzed. These results are discussed in future sections.

Filtrate 1 is known as the crude oil. This consists of light, intermediate and heavy fractions. A small amount of this crude is weighed and stored separately to do composition analysis on it.

3.5. Product Distribution

The dry-weight (without any sample) of the empty reactor and stirrer is measured: 8g of sample and 136g of water is taken in each experiment as the reaction mixture. The combined weight of the reaction mixture and the dry-weight of the reactor is the new weight of the reactor with the substance before the HTL reaction is performed.

Once the HTL process has been completed, the reactor has been cooled down and the internal pressure has reduced, the combined weight is measured again. The weight difference before and after the reaction is noted as the mass of gas produced during the HTL. This will be the yield of the first product produced (m_{gas}).

Once this weighing has been done, the liquid phase and the organic(solids) phase is transferred into 2 pre-weighed 250mL beakers as mentioned in the previous section. The beakers used are pre-weighed. The weight is of the beakers with the contents is measured and the weight of the empty beakers is subtracted to know the weights of each phase. This is followed by S-L separation where a moist filter cake (char) is obtained on a pre-weighed filter paper. Since the filter paper has been pre-weighed, weighing it with the filter cake presents the weight of the moist filter cake. After drying this cake and weighing it again, the weight of char produced from the experiment is obtained. This will be the yield of the second product produced (m_{char}).

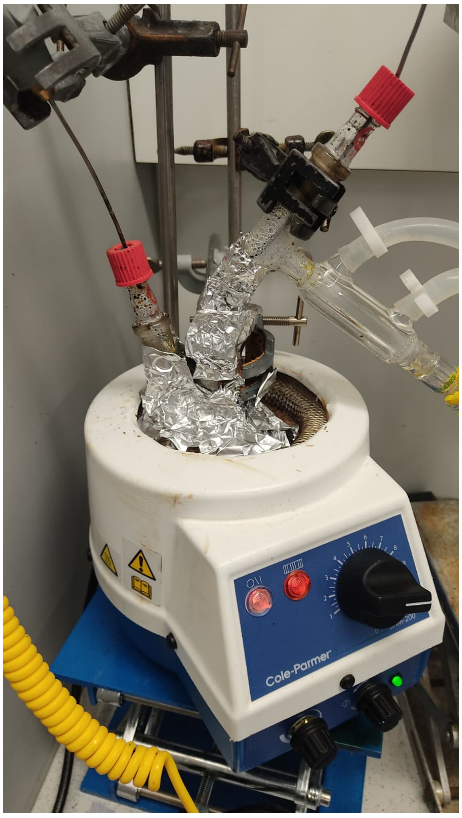


Figure 3.3: Distillation Setup

After the L-L separation and the evaporation of the water is complete in the rotary evaporator machine, the pre-weighed round-bottom flask containing the dried aqueous product is weighed. The dry weight of the round-bottom flask subtracted form this measured weight gives the weight of aqueous phase produced in each experiment. This will be the yield of the third product produced (m_{crude}).

The dry weight of the two-neck round-bottom flask subtracted from the weight of the two-neck round-bottom flask containing the crude after the first distillation step (performed at low temperatures to remove DCM) will result in the total weight of crude produced during each experiment. This will be the yield of the fourth product made. Once the second step of distillation is performed on this DCM free crude, the light fraction is collected in a small round-bottom flask and the weight is measured. Subtracting the dry-weight of this small round-bottom flask from the measured weight results in the weight of light fraction produced during each experiment (m_{light}). The weight of the remaining crude in the two-neck round-bottom flask will be the weight of the heavy fraction (m_{heavy}). The weight of the intermediate fraction would be the sum of weights of light and heavy fractions subtracted from the weight of the crude.

$$m_{\text{crude}} - (m_{\text{light}} + m_{\text{heavy}}) = m_{\text{intermediate}} \tag{3.2}$$

This is how the weights of each individual product is calculated. Finally the masses are tallied and ensured that the following equation is satisfied.

$$m_{\text{sample}} = m_{\text{gas}} + m_{\text{aqueous}} + m_{\text{crude}} + m_{\text{char}} \tag{3.3}$$

3.6. Characterization tests

The summary of this section is presented in a tabular format at the end of the discussion. The type of sample is abbreviated as follows: CH stands for char, AQ denotes aqueous product, LF and HF signify light-fraction and heavy fraction respectively. The sample name first consists the experiment conditions followed by type of sample.

3.6.1. Elemental Analysis

Samples: VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF were subjected to an elemental analysis study to determine the composition of carbon, nitrogen, hydrogen, and sulphur. An UNICUBE analyzer from Elementar Analysensysteme GmbH (Germany) was used for this purpose. 1-2mg of each sample was tightly packaged in a tin foil and combusted in the combustion tubes present inside the analyzer. The combustion was performed at 1800°C in the presence of oxygen (about 30mL/min). The analyzer was operated under the 'Graphite' mode in the 'C,H,N,S' setting. The final results were presented in terms of the percentages and analyzed in the future sections. [41] [49].

Figure 3.4: UNICUBE analyzer

3.6.2. Gas Chromatography-Mass Spectrometry

Gas Chromatography-Mass Spectrometry (GC-MS) was performed on the light fraction samples of: 340-60-LF, 310-60-LF, 340-35-LF, 310-35-LF to identify the organic compounds present in them. This analysis were conducted at the Department of Chemistry and Biochemistry at California State University, Los Angeles. The analyzer used is from Pegasus BTX GC-TOFMS series and the standard of measurement used was a mix of ASTM D7169 and ASTM D2887. Each sample, when analyzed over a long retention time, produces different peaks at different retention times. These peaks are then matched with the known peaks at a particular retention time from a database to identify the organic compounds present. The area of the peaks are then calculated to determine the concentration of each organic compound present in the given sample.

3.6.3. Inductively Coupled Plasma Optical Emission Spectrometry

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed on the samples: 340-60-AQ, 310-60-AQ, 340-35-AQ, 310-35-AQ to know their inorganic composition. SPECTRO AR-

COS ICP-OES machine from SPECTRO Analytical Instruments GmbH, Germany, was used for this purpose. About 0.1g of the samples were dissolved in about 5mL of hydrogen peroxide and loaded in the machine. The radial and axial measurements of the samples were noted and their compositions were determined [50].

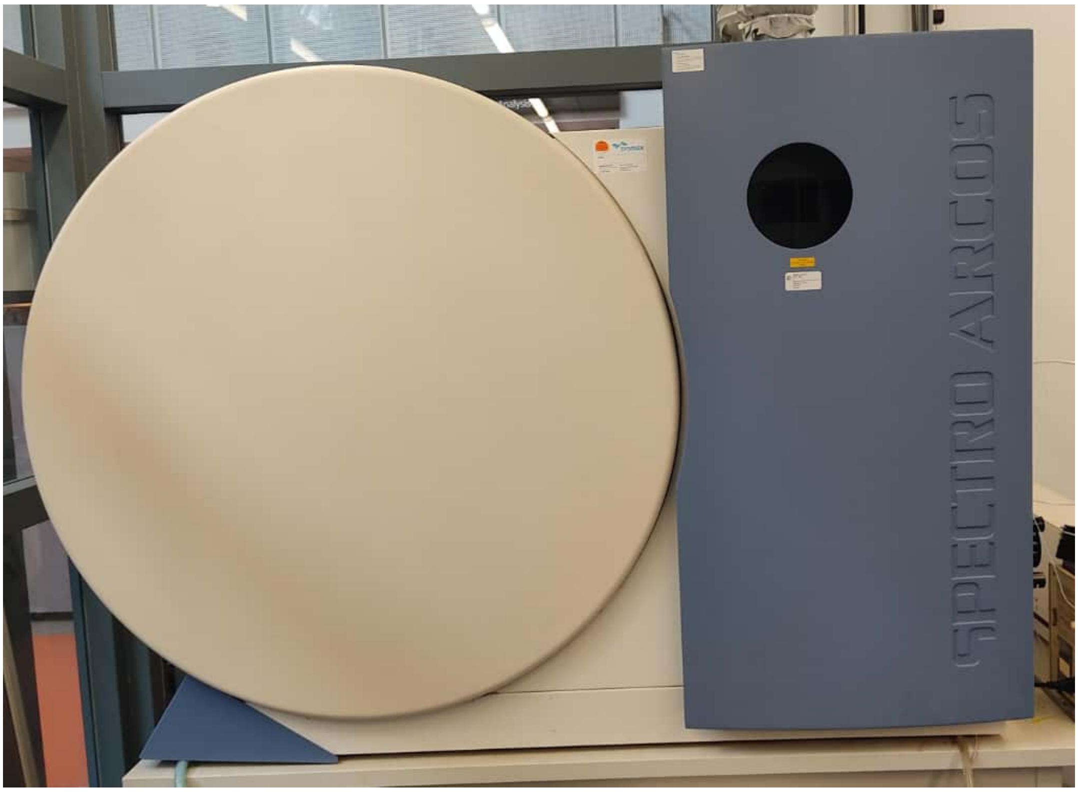


Figure 3.5: SPECTRO ARCOS ICP-OES

3.6.4. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed on the samples: VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF. The experiments was conducted in a SDT Q600 analyzer obtained from TA instruments company, United States of America. About 17mg of each sample were analyzed per run. 90µL ceramic cups were used to contain the samples. These cups ensure, inertness towards samples, ease of cleaning, and operations upto 1500°C. The samples were heated from room temperature to 105°C. Then the temperature was maintained isothermally for 10 minutes to remove any residual moisture. Post this, the heating was continued till 650°C and the samples were maintained at this temperature for 10 more minutes. After this the samples were cooled to 150°C at a rate of 20°C/minute and then let to cool by air convection down to room temperature. The heating rate was fixed at 10°C/minute for both the heating steps. The inertness of the environment was ensured by a constant flow of nitrogen (about 50mL/minute) [51] [4].

3.6.5. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was conducted on the samples: VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF, 340-60-LF, 310-60-LF, 340-35-LF, 310-35-LF, 340-60-CRUDE, 310-60-CRUDE, 340-35-CRUDE, 310-35-CRUDE. Nicolet iS50 FTIR Spectrometer from Thermo Fisher Scientific Inc. was used. The iS50 Average True Range (ATR) module was used for our analysis. The spectrometer was loaded with liquid nitrogen and calibrated. The ATR touch point is then activated. The samples were then loaded on the diamond crystal and proper contact between them were ensured using the pressure tip. 128 single measurement of each sample were taken and superimposed to obtain the final spectroscopy. The diamond crystal and the pressure tip were cleaned with isopropanol and the background spectroscopy was re-taken after samples[52].

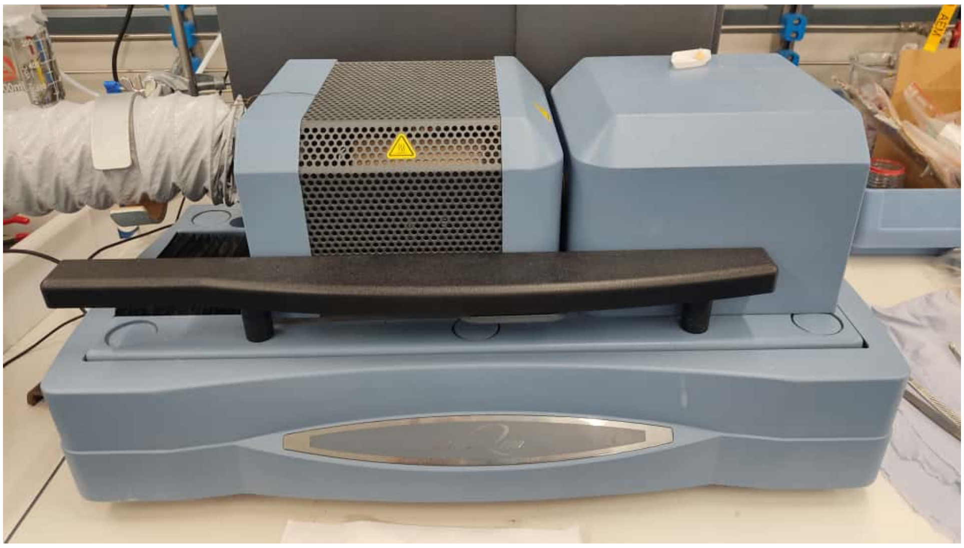
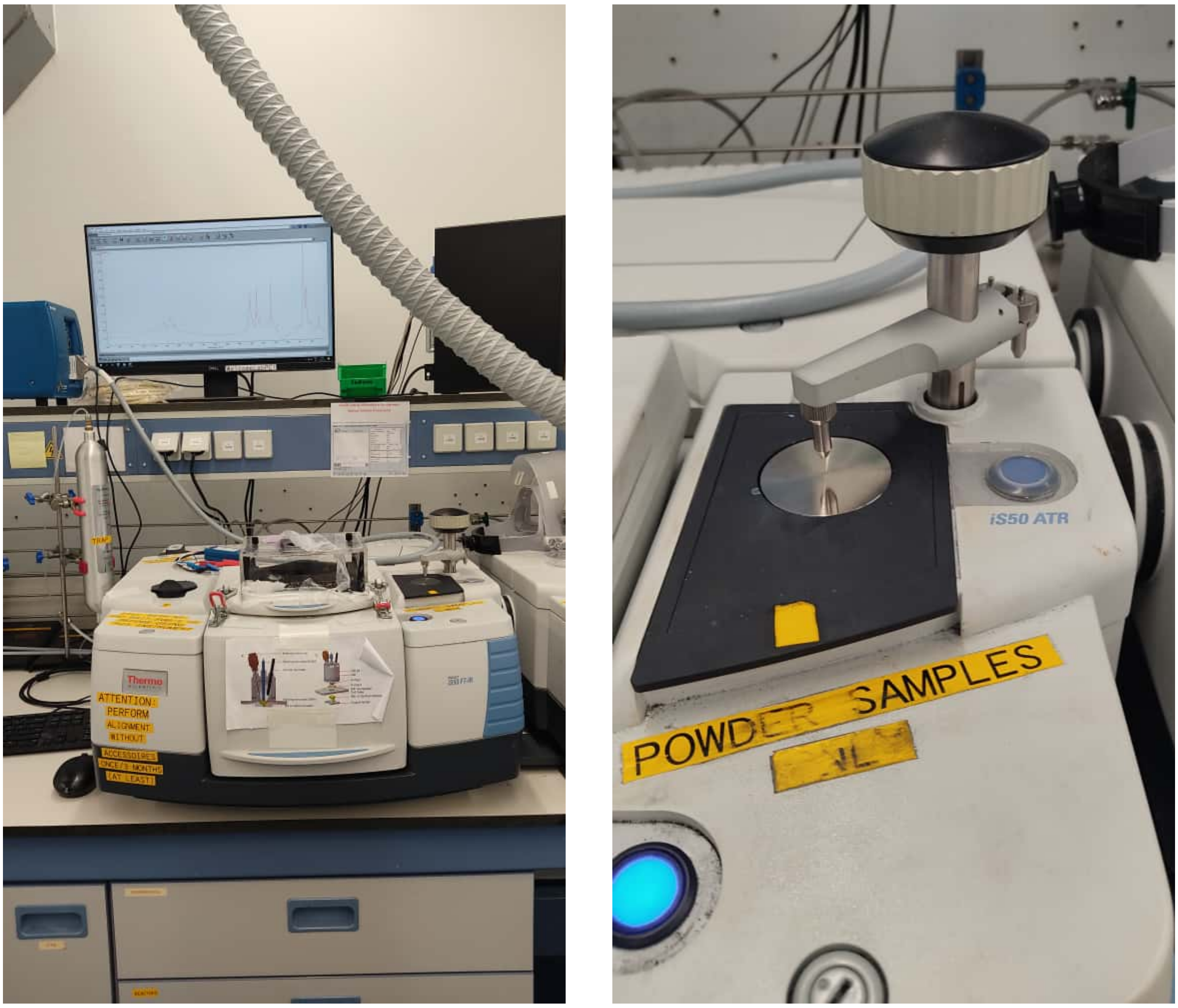


Figure 3.6: SDT Q600 analyzer



(a) Overall Setup-Nicolet iS50 FTIR Spectrometer

(b) Diamond crystal and pressure tip

Figure 3.7: FTIR Setup

Table 3.1: Characterization matrix of samples

Sample	Elemental	GC–MS	ICP–OES	TGA	FTIR
VR-RD	✓			✓	✓
340-60-CH	✓			✓	✓
340-60-HF	✓			✓	✓
310-60-CH	✓			✓	✓
340-35-CH	✓			✓	✓
340-35-HF	✓			✓	✓
310-35-CH	✓			✓	✓
310-35-HF	✓			✓	✓
340-60-LF		✓			✓
310-60-LF		✓			✓
340-35-LF		✓			✓
310-35-LF		✓			✓
340-60-AQ			✓		
310-60-AQ			✓		
340-35-AQ			✓		
310-35-AQ			✓		
340-60-CRUDE					✓
310-60-CRUDE					✓
340-35-CRUDE					✓
310-35-CRUDE					✓

4

Results and Discussion

4.1. Experimental Conditions

8g of sample and 136g of water were subjected to HTL. This is because only a limited quantity of VR-RD resin was provided, and it had to be rationed for all experiments. The sample:water (feed: solvent) ratio was kept at a constant 1:17. This was followed from Souza et.al, where they have also used the same ratio to perform HTL on various types of polymers [25]. This sample:water ratio was kept constant and not changed during the experiments. Due to time and material constraints (such as limited quantity), it was not considered as an experimental parameter to be tested.

Four experiments were conducted at two different temperature and residence time levels. The experiments are 1. 340°C-60 minutes (340-60) 2. 310°C-60 minutes (310-60) 3. 340°C-35 minutes (340-35) 4. 310°C-35 minutes (310-35). The original plan was to conduct 14 experiments at an additional lower level of 280°C and 10 minutes as well (included in A.1 section of Appendix). However, after the first experiment of 340-60, a lot of unreacted char and adhesive organic material were found in the reactor. This proved to be challenging to clean and required several additional steps beyond the standard bio-oil enrichment procedure (detailed in Section 3.4). After this discovery, it was decided not to pursue the lowest level of 280°C and 10 minutes. This was to prevent ineffective HTL, incomplete decomposition, and the intense/complicated clean-up process post-experiments at these low levels [7]. Since this study is about establishing a procedure to recycle vitrimer composites and resins, it was decided to focus on temperature and residence time levels, which were considered to be effective. Temperatures above 340°C took a very long time to reach in the reactor system and cool down. They also reached pressures of more than 150 bar, which were close to the pressure limit of the safety valve. The pressure reached was higher for longer residence times at the same temperature. Hence, to save time and to maintain the functionality of the reactor, temperatures above 340°C and residence times longer than 60 minutes were not tested. 35 minutes was considered a good middle point between 60 minutes and the planned initially lowest point of 10 minutes, therefore it was chosen.

Temperature decides many aspects of the reaction mechanism and conditions. At elevated temperatures, the pressure is also elevated. Although the effect of pressure on the experiment is assumed to be minimal, higher pressures result in a greater amount of water being retained in the liquid state and thus made available for HTL. 310°C falls under the aquathermolysis range of water. The stability of the H^+ and OH^- ions is better, and their interaction with the feed is the primary method of depolymerization and decomposition. The ionic reaction mechanism is dominant. These ions are the primary source for hydrogenation, and an enhanced H/C ratio in the HTL products can be expected(Chen). At 340°C, the HTL is operated closer to the thermal cracking range. The stability and concentration of H^+ and OH^- ions are compromised, and the presence of $H\cdot$ and $HO\cdot$ free radicals increase. Lesser hydrogenation from H^+ ions and elevated levels of cracking (due to elevated temperature) indicate a decreased H/C ratio in the HTL products [20]. The effect of conducting subcritical HTL under these two different mechanisms (temperatures) on the product yield and product composition will form a significant part of this study.

Residence time is an important parameter to study in any HTL study. It influences the yield and quality of the products. Increasing the residence time initially increases the yield of HTL products, as it provides sufficient time for proper contact and energy transfer between the materials and the solvent (water). However, after an optimal residence time, prolonging the residence time can lead to a decrease in product yield as it might trigger secondary conversion reactions, which can convert the products into secondary substances. Insufficient residence time could render the HTL purposeless and prevent it from forming any products. Hence, it is essential to experiment with different residence times to determine the optimal point for a particular material at a specific reaction temperature. The effect of conducting subcritical HTL under these two different residence times on the product yield and product composition will also form a significant part of this study [20].

4.2. Product Distribution

The way the product distribution has been performed and calculated has been detailed in section 3.5. The results are presented in Figure 4.1.

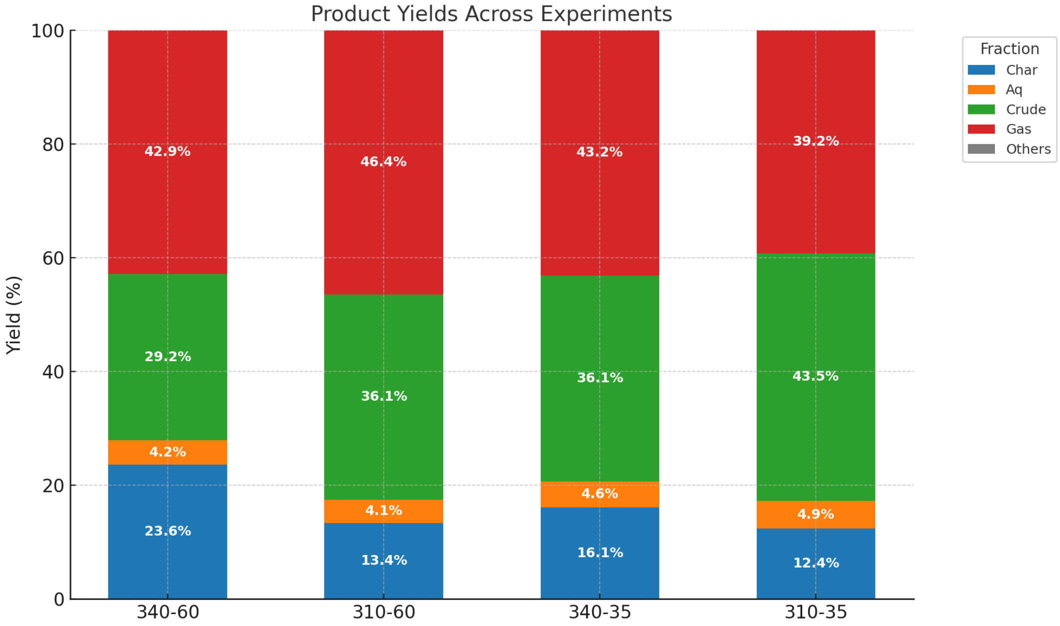


Figure 4.1: Product Distribution results

As mentioned in section 3.5, 8g of sample was taken for each experiment. The yield % of each type of product is calculated with respect to a reference weight of 8g. Gaseous product is one of the most significant products formed during the experiments. The lowest yield of gaseous product was obtained in experiment 310-35 (39.2% or 3.136g), meanwhile, the highest yield was obtained in experiment 310-60 (46.4% or 3.712g). The gaseous yields obtained from the experiments 340-60 and 340-35 seem to be about the same and between the highest and lowest yields. The yield of aqueous products was the lowest in all four experiments and did not vary much. Compared to the gaseous product yields, here the pattern is reversed. Experiment 310-35 produced the most aqueous product at about 4.9% (0.392g), and 310-60 produced the least aqueous product at about 4.1% (0.328g). However, the variance is not much, and overall, the yield of aqueous product in this study is considered to be very low. The yield of char was found to be the highest at 23.6% (1.888g) in experiment 340-60 and the lowest at 12.4% (0.992g) in experiment 310-35. The char yield seems to be fairly consistent in experiments 310-60, 340-35, and 310-35, but seems to spike in experiment 340-60. Finally, the yield of crude over the four experiments is analyzed. The highest yield of crude is observed in experiment 310-35 at 43.5% (3.48g), and the lowest yield of crude is observed in experiment 340-60 at 29.2% (2.336g). Experiments 310-60 and 340-35 produced the same yield of crude at 36.1% (2.888g).

The char is considered to be the VR-RD resin material, which was not broken down or reacted during the HTL process. It is preferred to minimize its yield when designing the HTL process. The gaseous product is also not preferred as it is not retrievable and might cause harmful air pollution to the surrounding environment. Since the gas couldn't be captured, its chemical composition was not analyzed. However, after the reactions were completed and the reactor was opened, a pungent odor was consistently observed. This is believed to be hydrogen sulphide (H_2S) or other sulphur-related gases which have been formed from the disulphide bonds present in 4-AFD. However, this couldn't be tested and confirmed. It is also theorized that the aniline could be converted to NH_3 and released as part of the gaseous mixture. Since a very minimal aqueous phase was produced, its complete composition couldn't be determined. Hence, suitable applications for it couldn't be ascertained. However, it is assumed that the aqueous material is composed of components that are inorganic in nature, as they don't dissolve in the organic solvents used. The crude is expected to either contain the individual constituents of the VR-RD resin or other organic compounds, which could be used as chemical feedstock or fuel. Therefore, the objective is to maximize the yield of the crude. In this regard, experiment 310-35 seems to be the most successful experiment, producing the highest yield of crude and the lowest yield of gaseous products and char.

These results conclude that the thermo-chemical degradation of the VR-RD resin is possible, in the form of subcritical HTL. The resin is degraded into four components: gas, aqueous, char, and crude. 310°C is more effective for the crude formation compared to 340°C. This indicates that during the subcritical HTL of VR-RD resin, the ionic reaction mechanism is more efficient than the aquathermolysis reaction mechanism. H^+ and OH^- ions depolymerize VR-RD resin better than $H\cdot$ and $HO\cdot$ free radicals. However, at 310°C, when the residence time is increased from 35 to 60 minutes, there is an onset of secondary conversion reactions, which convert the crude fractions to other products, such as gaseous products. This can be observed from a decrease in crude yield and an increase in gas yield from 310-35 to 310-60. Ahmad et.al report studies where higher temperature and residence time experiments resulted in the formed crude converting to char. Enhanced cracking of crude with higher carbon chains to compounds with lower carbon chains is also noted. This explains the relation between char yield % and temperature and residence time. This also explains the drop in crude yield % as the temperature and residence times are increased [21]. Although 340-35 is operated at a higher temperature and in a less efficient aquathermolysis mechanism, due to the lower residence time of 35 minutes, secondary conversion reactions are limited, and the crude yield is similar to 310-60. Lastly, 340-60 produces the lowest yield of crude due to being operated in a less efficient aquathermolysis mechanism and having significant secondary conversion reactions due to the higher residence time of 60 minutes [21]. Figure 4.2 showcases the product distribution of the different fractions within the crude.

The procedure for how each fraction is separated is detailed in section 3.4. Light fraction consists of crude components that have a boiling point of about 120°C. Intermediate fraction consists of crude components with a boiling point between 120 °C and 350°C. Heavy fraction consists of crude components with a boiling point greater than 350°C. These are the temperature classifications because the maximum obtainable temperature of the vapour and reaction medium were 120°C and 350°C, respectively. Light fraction vapour temperatures were monitored, and then these vapours were cooled over a condenser column and collected. The heavy fraction remained in the medium (two-neck round-bottom flask) and was collected once the distillation process was complete. The intermediate fraction was lost as vapours to the atmosphere. This is because it's vapours received enough thermal energy in the medium to vaporize but not enough to reach the condenser column. Hence, most of it was lost to the atmosphere, and some of it was recollected in the medium.

Light fractions are expected to contain gasoline-like compounds and light chemical intermediates. This could prove vital in upscaling HTL crude product into high-value chemicals. Intermediate fractions are also considered important due to their direct relevance to drop-in fuels such as diesel and kerosene. This represents a fraction which is believed to produce fuels with high heating value (HHV) [30]. However, it is not possible to test the composition and heating value of the intermediate fraction produced as its vapours are lost to the atmosphere. Heavy fractions are usually more challenging to upgrade and require more intensive processing, such as hydro-cracking, to be made into more desirable materials [7]. In this study, the heavy fraction formed resembled the char in particle appearance and texture. It is desirable to minimize the heavy fraction yield unless there are proven use cases for it.

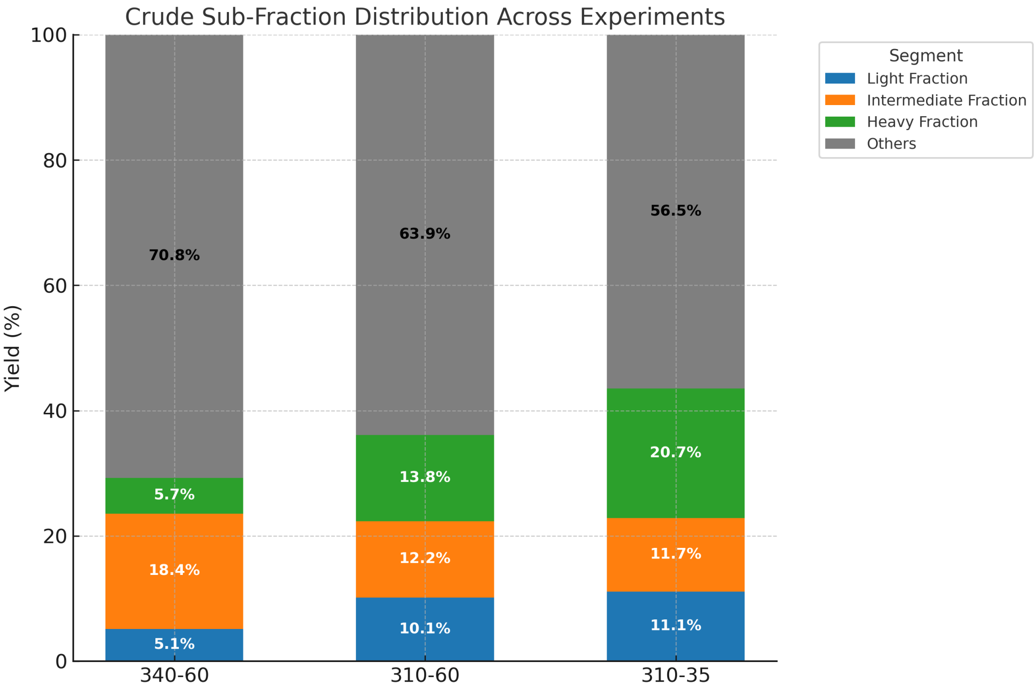


Figure 4.2: Product Distribution results-Crude

Experiment 310-35 produces the highest yield of light fraction at 11.1% (0.888g) and the highest yield of heavy fraction at 20.7% (1.656g). On the contrary, experiment 340-60 produces the lowest yield of light fraction at 5.1% (0.408g) and 5.7% (0.456g). The decline in the yield of light fraction from 310-35 to 340-60 can be explained by the significant increase in the secondary conversions. This could be converting the light fractions into compounds, which generally constitute the intermediate fraction region. As 310-35 produces the highest yield % of light fractions, it is considered to be desirable. A remarkable decrease in the yield of the heavy fraction as we increase the residence time from 35 minutes to 60 minutes at 310°C is noted. This could be explained by the additional residence time, which facilitates a better breakdown of heavier crude fractions into lighter fractions at 310°C. Lastly, the significant presence of intermediate fractions in 340-60 can be explained by the pronounced breakdown of the heavy fraction and the pronounced secondary conversion of the light fraction into intermediate fractions.

The crude sub-fraction distribution of experiment 340-35 is not shown, as there were some errors during weight measurement, and the mass balance was not satisfied.

4.3. Characterization test-Results

The results obtained from the different characterization tests that were conducted on the samples are presented and studied in this section. Further, inferences and conclusions are derived from these results.

4.3.1. Elemental Analysis

Elemental Analysis was conducted on the samples: VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF.

The results are presented in Figure 4.3.

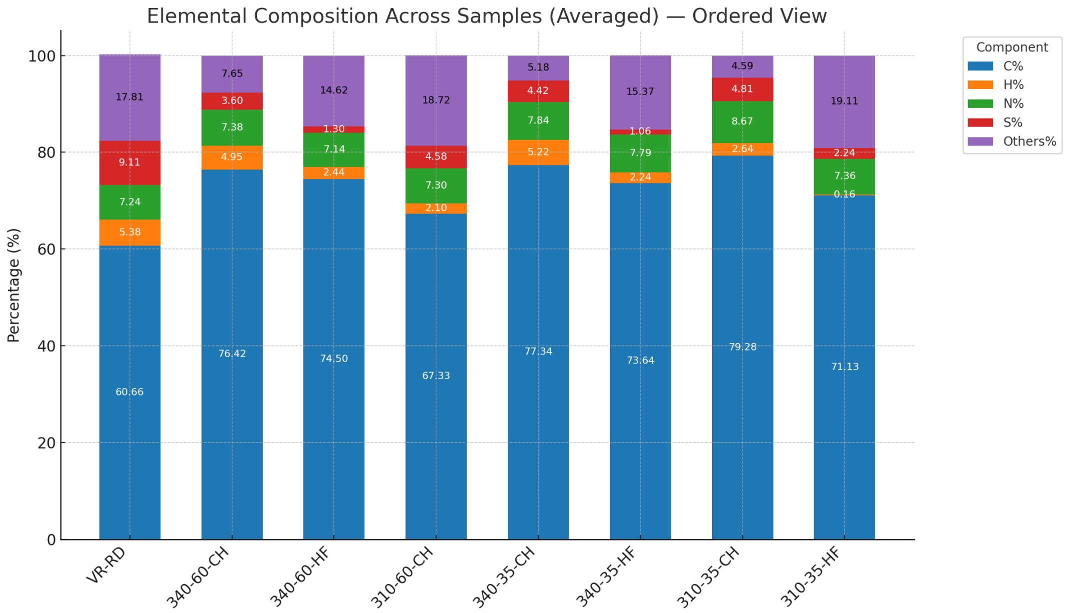


Figure 4.3: Elemental Analysis results

The composition of carbon has increased consistently across all the samples compared to VR-RD. The maximum increase is by 18.62% observed in 310-35-CH. Meanwhile, the lowest increase is by 6.67% observed in 310-60-CH. This indicates that, at the lower temperature setting of 310°C, the residence time greatly impacts the carbon content. Meanwhile, at the higher temperature setting of 340°C, the residence time doesn't seem to have much impact. This is indicated by the fact that 340-35-CH has only 0.92% carbon more than 340-60-CH. The source of carbon is determined to be from the components of VR-RD. The increase in carbon can be explained by two phenomena: The first is the loss of other elements, which in turn increases the composition of carbon. This is explained in the next paragraphs, especially regarding the loss of sulphur. The second phenomenon is the increase in the carbon content (or becoming condensed with carbon) due to the hydrothermal liquefaction itself. This is explained by the increased concentrations of H^+ and OH^- which promote reactions such as hydrolysis, dehydration, and decarboxylation. Most condensed products are partitioned to the solid (CH), yielding higher carbon content and lower heteroatom content than the heavy oil (HF). This behaviour is consistent with the observed ordering of carbon percentage at each condition (CH > HF). This results in char and heavy fraction becoming condensed with carbon. To further understand this, the detailed mechanism of how hydrothermal liquefaction breaks a material down needs to be understood. This requires further studies. It is also observed that the effect of residence time is more profound at 310°C rather than 340°C.

The composition of sulphur has decreased consistently across all the samples compared to VR-RD. The maximum decrease is by 8.05% observed in 340-35-HF. The maximum decrease in a char sample is observed in 340-60-CH (about 5.51%). Meanwhile, the lowest decrease is by 4.3% observed in 310-35-CH. The presence of sulphur can be explained by the disulphide groups present in the component 4-AFD. The loss in sulphur concentration can be attributed to the formation of SO_4 in the aqueous phase and the presence of sulphur in the gaseous phase. There are no conclusive tests that can be performed on the gaseous product, as it is lost in the ventilation. However, a particular rotten smell was observed, which suggests the presence of sulphur as H_2S in the gaseous product.

The composition of nitrogen seems to be fairly consistent and about the same composition compared to VR-RD, except for 310-35-CH, where a 1.43% increase is noted. The presence of nitrogen can be explained by the nitrogen atoms (aniline) present in the components of VR-RD. Since nitrogen is quite inert and doesn't react with other compounds even at high temperatures, its composition remains largely unchanged.

4.3.2. Gas Chromatography-Mass Spectrometry

Gas Chromatography-Mass Spectrometry (GC-MS) was conducted only on the samples 340-60-LF, 310-60-LF, 340-35-LF, 310-35-LF. This is because the crude samples were determined to be too viscous for the spectrometer to handle.

The results of the spectroscopy study are presented in the Figures 4.4 and 4.5:

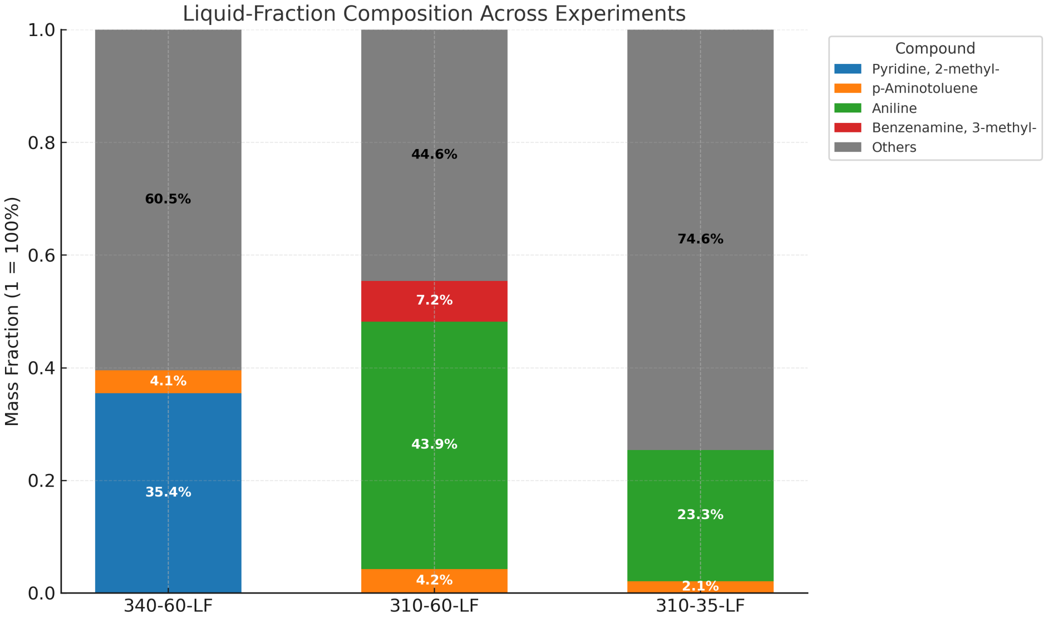


Figure 4.4: GC-MS results

These results confirm the presence of aniline in three out of the four experiments performed. This is expected as 4,4' -methylenebis[N, N-bis(2,3-epoxypropyl)aniline], which forms the principal constituent of VR-RD, is an aniline component. This result confirms that the VR-RD matrix has been chemically broken and the constituents have been separated. This circumstance strongly indicates the viability of hydrothermal liquefaction as a chemical recycling method for VR-RD and other forms of Vitrimer Resins.

Experiment 310-60 yields the highest aniline content at 43.9%. It also produced a significant 7.2% of 3-methyl-benzenamine and 4.2% of p-Aminotoluene. Experiment 310-35 produces the next highest concentration of aniline at 23.3%. It also produced p-Aminotoluene at 2.1%. Hence, it can be inferred that the optimum temperature for recovering the primary and most valuable starting material is at 310°C, where the ionic reaction mechanism takes place. It can also be observed that a longer residence time of 60 minutes at the same temperature is required for the maximum recovery of 4,4' -methylenebis[N,N-bis(2,3-epoxypropyl)aniline]. At 310°C, 35 minutes is insufficient for complete depolymerization. Hence, if aniline recovery was the main objective, 310-60 would be the most optimum point [24][20].

Negligible or almost no aniline was produced in the experiments conducted at the higher temperature setting of 340°C. This is quite an interesting result, and a few things could potentially be happening: 1. At this temperature, the aniline is getting converted to other compounds, such as 2-methyl-pyridine (as in experiment 340-60). Due to the high temperature, secondary conversion reactions occur, resulting in a multitude of organic compounds. A longer residence time of 60 minutes converts most of the already converted organic compounds into Pyridine, 2-methyl. These results lead to the conclusion that more severe recombination/cyclization of nitrogen-containing compounds occurs 340-60. 2. The spectrometer is not able to detect most of the aniline produced, and it might be present in the undetectable 'Others' compounds. This could occur if the inlet/transfer temperature of the machine is not proper or the method used to match the compounds is not accurate. However, the chance of this error is minimal as the machine has handled a variety of organic compounds with a proven track record. The conversion of aniline to secondary compounds is the more plausible explanation [20] [21].

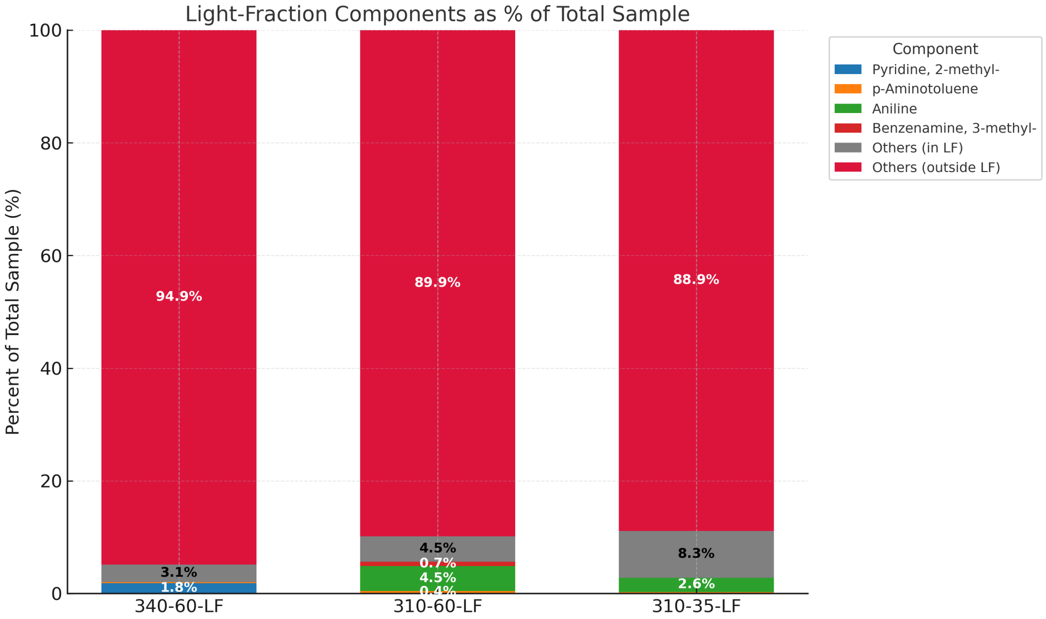


Figure 4.5: GC-MS results

4.3.3. Inductively Coupled Plasma Optical Emission Spectrometry

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed on the samples 340-60-AQ, 310-60-AQ, 340-35-AQ, 310-35-AQ to determine their inorganic compounds composition. It was not possible to perform ICP-OES on VR-RD as it doesn't dissolve in Hydrogen Peroxide or in Aqua Regia. The char and heavy fraction samples don't dissolve in the before mentioned solvents and hence were not included for this study. The crude and the light fraction samples consisted a majority of organic compounds which were analyzed using the other techniques discussed in this section. Hence, ICP-OES was conducted only on the aqueous samples. Since only about 0.32g of Aqueous samples were produced per experiment, this was the only study conducted on them. The objective was to observe a trend in the composition of the samples as the experimental conditions were varied and come up with inferences from the results.

The results are presented in Figure 4.6.

The 4 major components present in the aqueous phase are: Calcium (Ca), Chlorine (Cl_2), Phosphate (PO_4), and Sulphate (SO_4). The production of SO_4 is the most interesting as its source can be directly traced back to the sulphur present in 4-AFD in its disulphide component. It can be theorized that the S-S and C-S bonds present are broken and the available S oxidizes in the presence of residual oxygen present and forms the SO_4 in the Aqueous phase (ref source for this).

The formation of SO_4 seems to be constant at the higher temperature setting of 340°C regardless of the residence time. This is because at such high temperature, the energy to break the bonds is abundant and the bonds are broken almost instantly. However, at the lower temperature setting of 310°C, we see a direct relationship between the residence time of the experiment and the concentration of SO_4 formed. The concentration of SO_4 seems to be proportional to the residence time, indicating the lesser energy provided at 310°C for the bonds to break.

The other interesting result from this study is the high concentration of Cl observed in each sample. This is not explicitly understood as there are no apparent sources of Cl in VR-RD and its components. However, it can be theorized that the Cl present in DCM contributed to this. The concentration of Cl is directly proportional to the residence time of the experiment at the higher temperature setting of 340°C and inversely proportional to the residence time of the experiment at the lower temperature setting of

310°C. If use cases are developed for the aqueous phase product then this contamination of Cl from DCM would be a problem to be fixed.

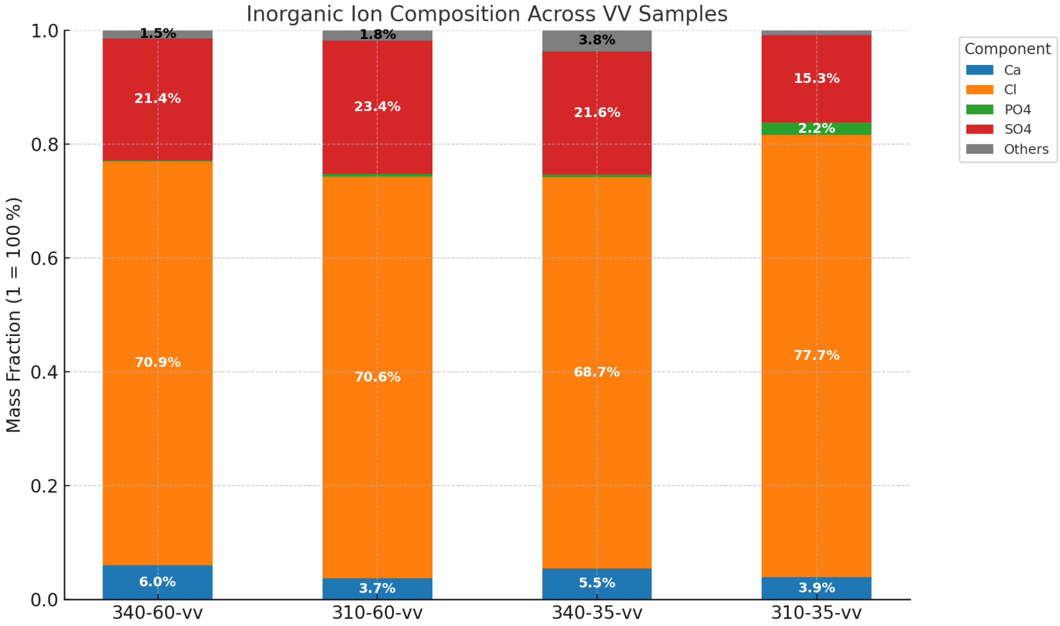


Figure 4.6: ICP-OES results

4.3.4. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) were performed on the following samples: samples: VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF. The TGA study was conducted as attempt to determine the material properties of the produced char and heavy fraction in comparision to VR-RD. Since the char is unreacted VR-RD, it is important to determine the change in the material property after the process. However, since the materials being analyzed here are already cured materials, TGA is performed to determine the thermal stability. It is important to note that TGA and Differential Scanning Calorimetry (DSC) are usually performed to analyze the degree of cure in a resin system.

The weight vs temperature is recorded from 105°C. This is acts as a drying step which ensures accurate results. $T_{2.5\%}$ and $T_{5\%}$ are the temperatures at which 2.5% and 5% of the mass is lost post heating. In the char samples, 340-35-CH has the lowest $T_{2.5\%}$ and $T_{5\%}$ and 310-60-CH has the highest $T_{2.5\%}$ and $T_{5\%}$. The $T_{5\%}$ of 310-60-CH is even higher than that of VR-RD at about 300°C. The heavy fraction samples have significantly lower $T_{2.5\%}$ and $T_{5\%}$ temperatures. This clearly indicates that they are not the same material as char and are some other materials which have been extracted from the crude.

The results of TGA are presented in Fig 4.7 and 4.8.

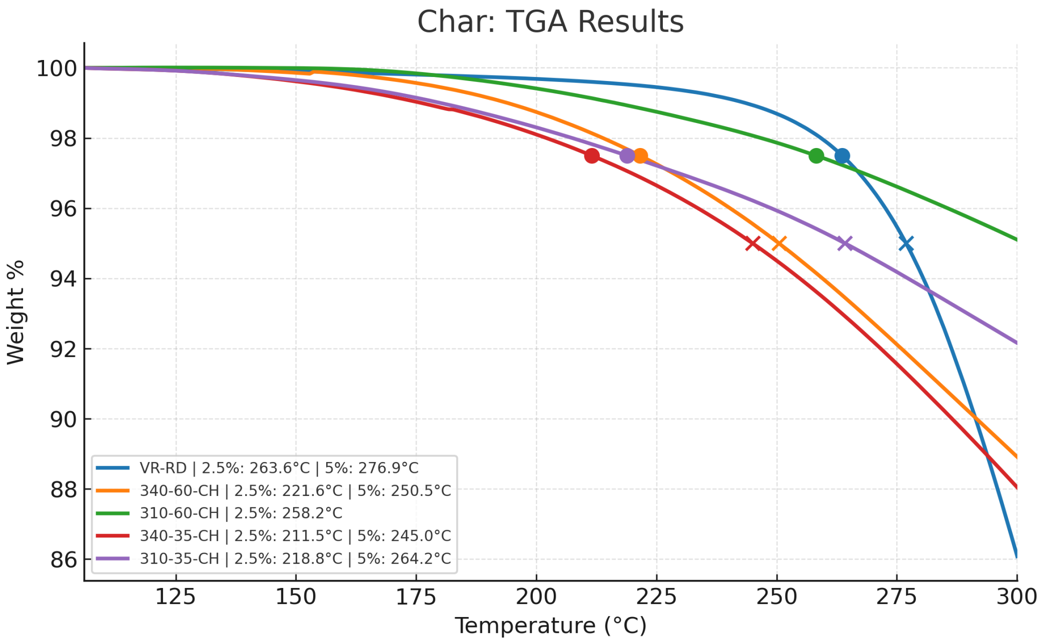


Figure 4.7: Char-TGA

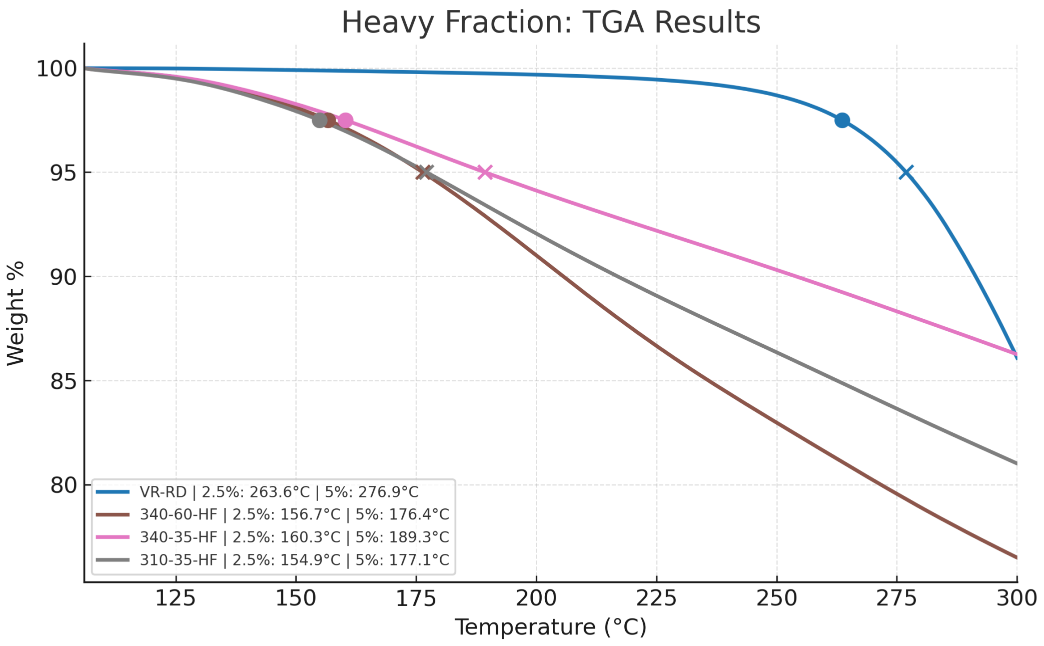


Figure 4.8: Heavy Fraction-TGA

4.3.5. Fourier Transform Infrared Spectroscopy

Samples VR-RD, 340-60-CH, 340-60-HF, 310-60-CH, 340-35-CH, 340-35-HF, 310-35-CH, 310-35-HF, 340-60-LF, 310-60-LF, 340-35-LF, 310-35-LF, 340-60-CRUDE, 310-60-CRUDE, 340-35-CRUDE, 310-35-CRUDE were subjected to Fourier Transform Infrared Spectroscopy (FT-IR). Since these samples have never been produced before, FT-IR has never been performed on them and there are no references to compare. FT-IR on VR-RD has also never been performed before. The objective was to characterize the new materials formed chemically by identifying the compounds and functional groups present in them. The results of the FT-IR are showcased below:

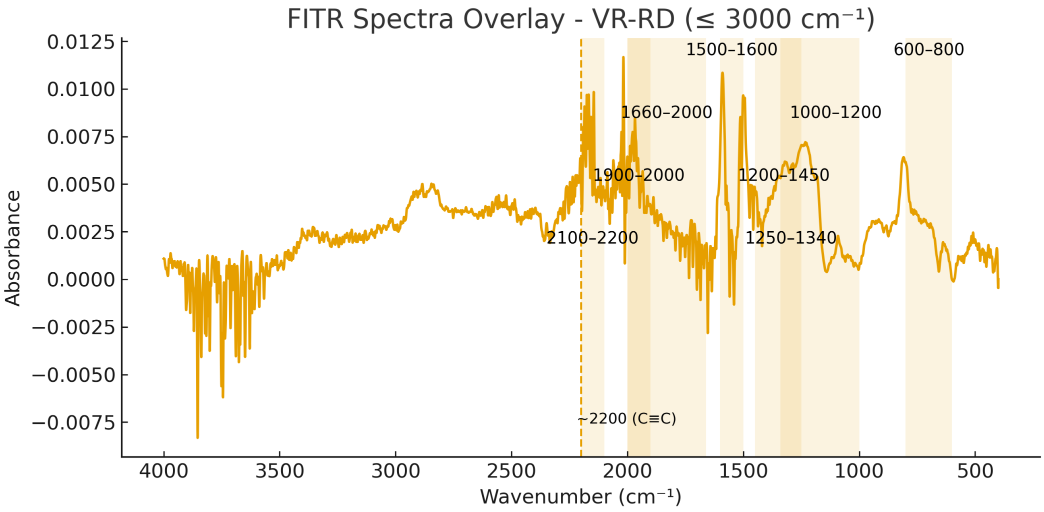


Figure 4.9: FTIR VR-RD

The notable peaks of VR-RD spectrum are at broad range from 1200-1450 (cm^{-1}), 1500-1600 (cm^{-1}), 1900 to 2000 (cm^{-1}), and 2100-2200 (cm^{-1}). There are also minor peaks from 600-800(cm^{-1}). Since there are peaks at about 2200 (cm^{-1}) followed by peaks at 600-800 (cm^{-1}), 1000-1200 (cm^{-1}) and 1300-1600 (cm^{-1}), there is a strong indication of the presence of C≡C. The presence of peaks from 1500-1600 (cm^{-1}) indicate C=C-C Aromatic ring stretch and the peaks from 1660-2000 (cm^{-1}) indicate presence of multiple Aromatic combination bands. Lastly, the presence of broad peaks from 1250-1340 1500-1600 (cm^{-1}) indicate the presence of Aromatic secondary amines (aniline) [46].

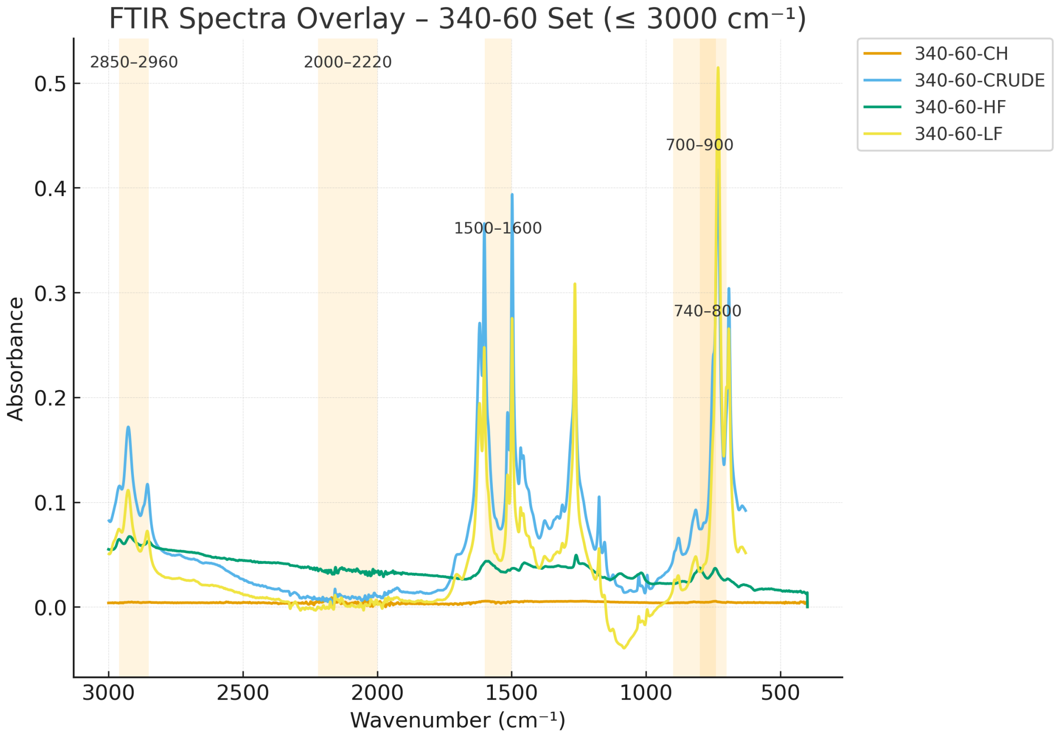


Figure 4.10: FTIR 340-60

The notable peaks of 340-60-CH are from 2000 to 2220 (cm^{-1}) and few minor peaks from 700-900(cm^{-1}) and from 1500-1600 (cm^{-1}). These indicate presence of C≡C both Terminal and Medial alkynes. Lastly, primary and secondary amines present (NH stretch), cynaide, thiocyanate, and related ions. The notable sharp peaks of 340-60-HF are 740 to 800, 1260, 1452, 1587 $\tilde{2}$100, 2850-2960 (cm^{-1}). These indicate long chain linear aldehyde compounds, C≡C terminal alkynes, open-chain imino compounds, isothiocynate, carboxylate, and secondary amines.The noise of the spectra data is significantly lower in the crude and light fraction samples. Hence, it becomes easier to identify the peaks. The notable peaks of 340-60-CRUDE are: 691, 732, 1264, 1466, 1497, 1515, 1601, 1618, 2854, 2926 (cm^{-1}). These indicate long chain linear aldehydes, methylene (C-H bend), secondary amine, aromatic primary amine (aniline), primary amine, carbonate ions, thiols, organic phosphates, and open-chain imino compounds. The spectra data and peaks of 340-60-LF are quite similar to that of 340-60-CRUDE with a notable decrease of peaks 2854 and 2926 (cm^{-1}). This indicate a significant decrease in the concentration of aldehyde compounds in the light fraction compared to the crude, However, the other mentioned compounds and functional groups for 340-60-CRUDE will also be present in 340-60-LF [46].

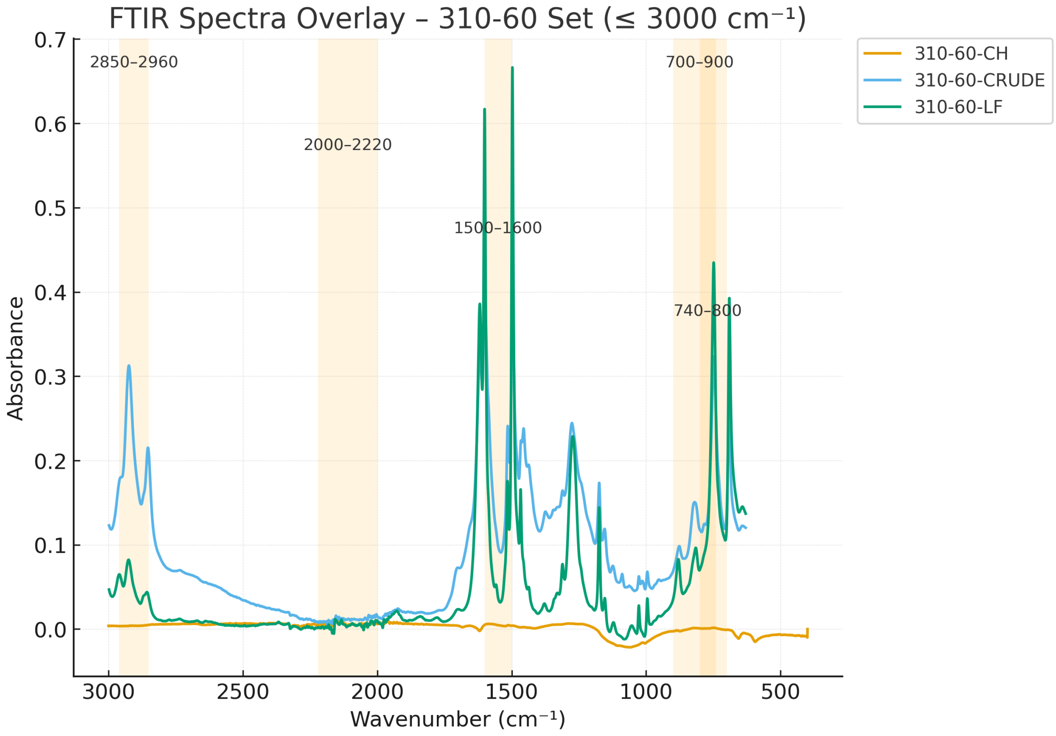


Figure 4.11: FTIR 310-60

The notable peaks of sample 310-60-CH lie in the range of 2000 to 2200 (cm^{-1}). These indicate presence of C≡C both Terminal and Medial alkynes. Lastly, primary and secondary amines present (NH stretch), cynaide, thiocyanate, and related ions. The spectra data for this char sample is quite noisy and it is tough to find exact peaks. Hence, a range of peaks is considered. The notable peaks of 310-60-CRUDE are 691, 748, 1276, 1455, 1497, 1514, 1601, 1618, 2853, 2924 (cm^{-1}). 310-60-LF also has the same peaks except 2853 and 2924 (cm^{-1}). These indicate long chain linear aldehydes, methylene (C-H bend), secondary amine, aromatic primary amine (aniline), primary amine, carbonate ions, thiols, organic phosphates, and open-chain imino compounds.The spectra data and peaks of 310-60-LF are quite similar to that of 310-60-CRUDE with a notable decrease of peaks 2854 and 2926 (cm^{-1}). This indicate a significant decrease in the concentration of aldehyde compounds in the light fraction compared to the crude, However, the other mentioned compounds and functional groups for 310-60-CRUDE will also be present in 310-60-LF [46].

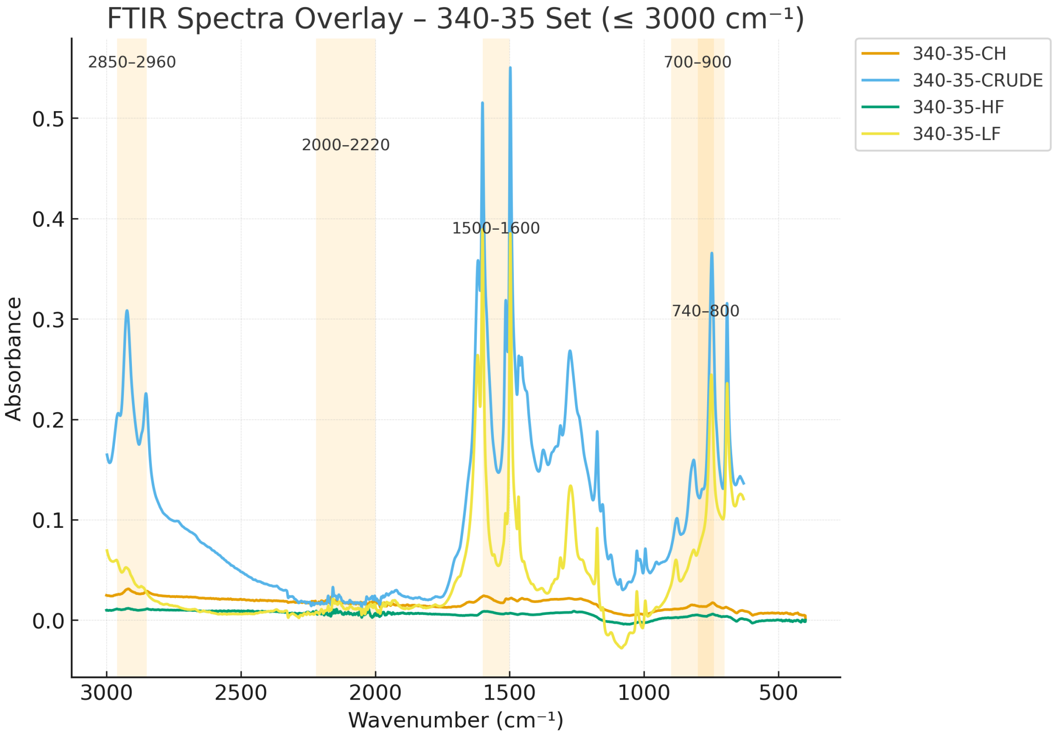


Figure 4.12: FTIR 340-35

The notable peaks in 340-35-CH are 750, 1278, 1454, 1494, 1596, 1989, 2162, 2848, 2918 and 3040 (cm^{-1}). These indicate the presence of linear long chain aldehydes, methylene (C-H bend), aromatic C-H in-plane bend, secondary amines, open-chain azo, open-chain imino, and isothiocyanate compounds. The notable peaks in 340-35-HF are 629, 947, 1590, 2024, 2144, 2158, 2847, 2918 (cm^{-1}). These indicate the presence of linear long chain aldehydes, methylene, aromatic C-H in-plane bend, secondary amines.The notable peaks of 340-35-CRUDE are 690, 749, 1174, 1273, 1467, 1497, 1600, 1618, 2852, 2923 (cm^{-1}). 340-35-LF also has the same peaks except 2852 and 2923 (cm^{-1}). These indicate long chain linear aldehydes, methylene (C-H bend), secondary amine, aromatic primary amine (aniline), primary amine, carbonate ions, thiols, organic phosphates, and open-chain imino compounds.The spectra data and peaks of 340-35-LF are quite similar to that of 340-35-CRUDE with a notable decrease of peaks 2854 and 2926 (cm^{-1}). This indicate a significant decrease in the concentration of aldehyde compounds in the light fraction compared to the crude, However, the other mentioned compounds and functional groups for 340-35-CRUDE will also be present in 340-35-LF [46].

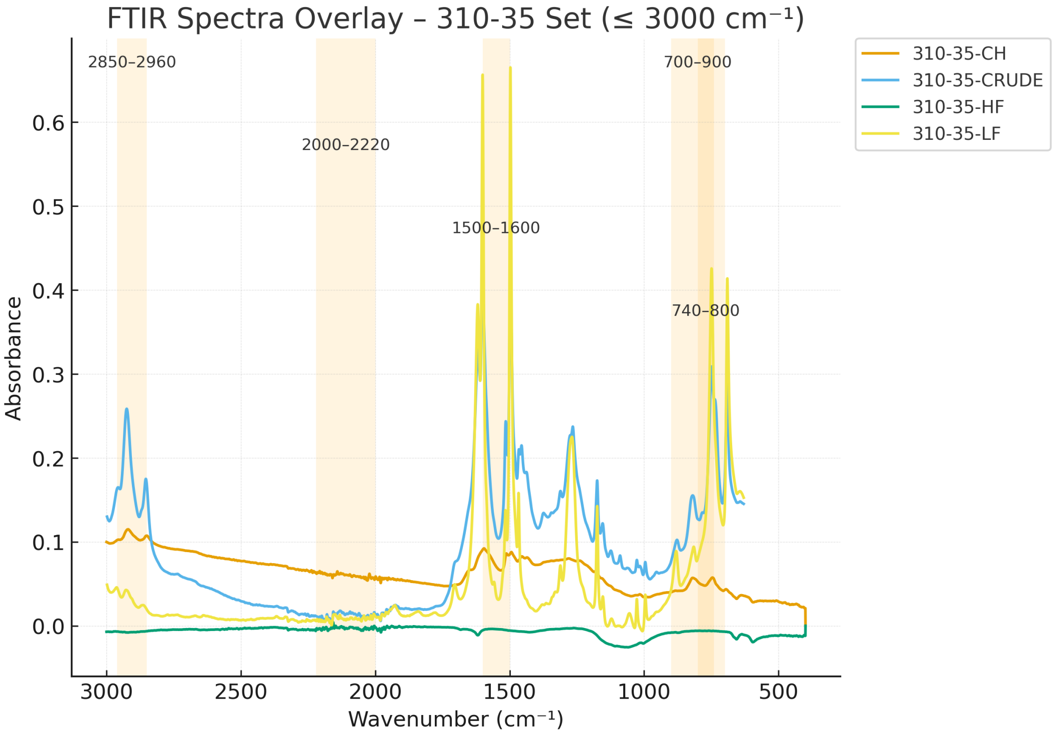


Figure 4.13: FTIR 310-35

The notable peaks of 310-35-CH are 745, 820, 2021, 2141, 2919 (cm^{-1}). These peaks correspond to the following compounds: long chain linear aldehydes, methylene, cyanide ions, thiocynate ions, peroxides.The notable peaks of sample 310-35-HF lie in the range of 2000 to 2200 (cm^{-1}). These indicate presence of C≡C both Terminal and Medial alkynes. Lastly, primary and secondary amines present (NH stretch), cynaide, thiocyanate, and related ions. The spectra data for this char sample is quite noisy and it is tough to find exact peaks. Hence, a range of peaks is considered. The notable peaks of 310-35-CRUDE are 691, 748, 1265, 1456, 1497, 1514, 1601, 1618, 2853, 2924 (cm^{-1}). 310-35-LF also has the same peaks except 2853 and 2924 (cm^{-1}). These indicate long chain linear aldehydes, methylene (C-H bend), secondary amine, aromatic primary amine (aniline), primary amine, carbonate ions, thiols, organic phosphates, and open-chain imino compounds.The spectra data and peaks of 310-35-LF are quite similar to that of 310-35-CRUDE with a notable decrease of peaks 2854 and 2926 (cm^{-1}). This indicate a significant decrease in the concentration of aldehyde compounds in the light fraction compared to the crude, However, the other mentioned compounds and functional groups for 310-35-CRUDE will also be present in 310-35-LF [46].

Compared to crude and LF, CH and HF show very less absorbance. Crude and LF seem to have a very similar spectroscopy across the four experiments. The missing compounds in LF compared to crude are aldehydes which have been separated from the LF during the distillation process. Both crude and LF seem to have strong aromatic cores (dual peaks at 1500-1600 (cm^{-1})). Similar dual peaks at 1500-1600 (cm^{-1}) is observed in the paper Schenk et.al where 4,4′-methylenebis[N,N-bis(2,3-epoxypropyl)aniline] is also the epoxy agent for the vitrimer resin. Hence, this confirms the GC-MS findings that the common epoxy agent, 4,4′-methylenebis[N,N-bis(2,3-epoxypropyl)aniline], has been successfully recovered after the HTL of VR-RD [53].

5

Conclusion

This study presented a detailed approach to initiate research on recycling vitrimer composites using thermo-chemical conversion methods. The primary investigation of this study was to analyze the effects of performing sub-critical Hydrothermal Liquefaction (HTL) on Vitrimer Resin (VR-RD) and the decomposition of the resin. Chemical breakdown of VR-RD and the synthesis of new chemicals were observed in all four experiments conducted. This answers the first research question posed. VR-RD was broken into four primary components. They are 1. Gaseous product, 2. Crude, 3. Char, 4. Aqueous Product. Crude was further subdivided into 1. Light fraction, 2. Intermediate fraction, and 3. Heavy fraction. This was performed using fractional distillation. All four experimental conditions tested were successful in recycling the vitrimer resin. Hence, the second research question posed was also answered. The light fraction present in the crude was one of the most important products obtained. The highest yield of light fraction was obtained in experiment 310-35. This was about 11.1% of the initial resin feed. This experimental condition was considered to be the most optimal as it produced the highest yield of light fraction for the least amount of temperature and residence time. This would be the answer for the third research question posed at the start of this project. Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the composition of VR-RD and then the composition of each product produced. The formation of new compounds and functional groups was observed. The gaseous product was not analyzed as it is not obtainable and is lost in the fume hood. Gas Chromatography-Mass Spectrometry (GC-MS) showed the formation of Aniline in the light fraction of the crude formed. This implies that the epoxy agent EP 600 Part A has been either fully or partially separated and recovered during the process. This can be retrieved and used to re-manufacture vitrimer resin or used as chemical feedstock for other processes. These results further corroborated the conclusion that HTL broke down the VR-RD resin and recycled it under all the tested conditions.

This work concluded that subcritical HTL of Vitrimer Resin VR-RD is possible and that VR-RD can be broken down chemically. All the research questions that were posed at the start of this project have been answered successfully. This study also concludes that this is a promising field to continue research on. Since this work is quite novel and has never been done before, it was filled with a lot of surprises and learning. This contributed to many recommendations for a better continuation of this study. These recommendations are presented in the next section.

6

Recommendations

In light of these results and conclusions, the following recommendations for future experiments and design work are recommended.

- Since the optimal condition with regards to the light fraction yield was at the lowest tested condition (310°C and 35 minutes), it is recommended to test experimental conditions lower than this. This might increase the yield of the light fraction. The lower limit (temperature or residence time below which Hydrothermal Liquefaction (HTL) becomes inefficient) needs to be determined. Also using a lower temperature is benefical in reducing the energy demand for the process making it financially attractive.
- A catalyst such as KOH or 1-Thioglycerol could increase the yield of the fraction or the crude itself. This is because these chemicals enhance the presence of H^+ and OH^- ions which enhance the depolymerization. It is recommended to test the efficiency of HTL using catalyst and noting the difference in yield%.
- Another recommendation is noting the results of all the experiments performed to analyze the dependence of one factor or experimental parameter on the other. This could be done using the Response Surface Methodology (RSM) statistical tool. This would be useful in finding the optimum point when multiple parameters are considered [54].
- Once the above mentioned recommendations have been implemented, the most optimum condition could be repeated for the vitrimer composite and the recovery of the carbon fibers from the VR-RD resin, could be studied. This also includes comparing the properties of the recovered fibers to that of a new one.
- Once a more detailed and refined process has been developed for Vitrimer Composites, further studies such as Techno-Economic Assessment (TEA), Life Cycle Analysis (LCA) could be conducted to further develop the business case for it. The process can be scaled up to pilot scale and compare with other recycling methods for fibre reinforced composite resin systems.

References

[1] Valco Group. *Epoxy Resins — Manufacturing Process of Epoxy Resins*. URL: `https://www.valcogroup-valves.com/faq-2/epoxy-resins-manufacturing-process-of-epoxy-resins/` (visited on 09/15/2025).

[2] Naheed Saba et al. “Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications”. In: *Journal of Reinforced Plastics and Composites* 35.6 (2016), pp. 447–470.

[3] European Composites Industry Association (EuCIA). *EuCIA: Background document on circular economy*. Background document. Version 002. Brussels, Belgium: European Composites Industry Association, Nov. 2022. URL: `paste%20the%20PDF%20or%20landing-page%20URL%20here` (visited on 09/07/2025).

[4] Niklas Lorenz, William E Dyer, and Baris Kumru. “High-Performance Vitrimer Entailing Renewable Plasticizer Engineered for Processability and Reactivity toward Composite Applications”. In: *ACS Applied Polymer Materials* 7.3 (2025), pp. 1934–1946.

[5] Sudheer Kumar, Sukhila Krishnan, and K Prabakaran. “Renewable resource-based epoxy vitrimer composites for future application: A comprehensive review”. In: *ACS Sustainable Resource Management* 1.9 (2024), pp. 2086–2107.

[6] Esteban Ocampo et al. “Hydrothermal liquefaction process: Review and trends”. In: *Current Research in Green and Sustainable Chemistry* 7 (2023), p. 100382.

[7] Judit Sandquist, Roman Tschentscher, and Gonzalo del Alamo Serrano. “Hydrothermal liquefaction of organic resources in biotechnology: how does it work and what can be achieved?” In: *Applied microbiology and biotechnology* 103.2 (2019), pp. 673–684.

[8] Luis Cutz et al. “Exploring the catalytic hydrothermal liquefaction of Namibian encroacher bush”. In: *Scientific Reports* 15.1 (2025), p. 112.

[9] Market Intelo. *Vitrimer Market Research Report 2033*. URL: `https://marketintelo.com/report/vitrimer-market` (visited on 09/07/2025).

[10] Mordor Intelligence. *Epoxy Resin Market Size & Share Analysis — Growth Trends & Forecasts (2025–2030)*. June 13, 2025. URL: `https://www.mordorintelligence.com/industry-reports/global-epoxy-resin-market-industry` (visited on 09/07/2025).

[11] Vincent Schenk et al. “Vitrimer composites: current status and future challenges”. In: *Materials Advances* 3.22 (2022), pp. 8012–8029.

[12] Hafeezullah Memon, Yi Wei, and Chengyan Zhu. “Recyclable and reformable epoxy resins based on dynamic covalent bonds–Present, past, and future”. In: *Polymer Testing* 105 (2022), p. 107420.

[13] Christopher J Kloxin et al. “Covalent adaptable networks (CANs): a unique paradigm in cross-linked polymers”. In: *Macromolecules* 43.6 (2010), pp. 2643–2653.

[14] Hechen Liu et al. “Rapid repair and degradation: A study of high-performance recyclable vitrimer epoxy resin based on disulfide bonds”. In: *Polymer Testing* 137 (2024), p. 108528.

[15] Hongwei Si et al. “Rapidly reprocessable, degradable epoxy vitrimer and recyclable carbon fiber reinforced thermoset composites relied on high contents of exchangeable aromatic disulfide crosslinks”. In: *Composites Part B: Engineering* 199 (2020), p. 108278.

[16] U.S. Environmental Protection Agency. *N,N-Dimethylformamide: Hazard Summary*. Hazard Summary. CASRN 68-12-2. Washington, DC: U.S. Environmental Protection Agency, Sept. 2016. URL: `https://www.epa.gov/sites/default/files/2016-09/documents/n-n-dimethylformamide.pdf` (visited on 09/08/2025).

[17] National Diagnostics. *Dithiothreitol (DTT) — Safety Data Sheet*. Safety Data Sheet EC-601. Version 3.0. National Diagnostics, Apr. 26, 2019. URL: `https://www.nationaldiagnostics.com/safety_data/sheets/EC-601.pdf` (visited on 09/08/2025).

[18] N Lorenz et al. "Characterization and modeling of an epoxy vitrimer based on disulfide exchange for wet filament winding applications". In: *Polymer Engineering & Science* 64.8 (2024), pp. 3682–3702.

[19] Min-Jung Ko, Hwa-Hyun Nam, and Myong-Soo Chung. "Subcritical water extraction of bioactive compounds from Orostachys japonicus A. Berger (Crassulaceae)". In: *Scientific Reports* 10.1 (2020), p. 10890.

[20] Zhong Chen. "New insight into subcritical and supercritical water reactivity during non-catalytic hydrothermal upgrading of heavy oil". In: *Fuel* 366 (2024), p. 131380.

[21] Fiaz Ahmad et al. "Reaction Mechanism and Kinetics of Hydrothermal Liquefaction at Sub-and Supercritical Conditions: A Review". In: *Biomass* 5.1 (2025), p. 9.

[22] Yan Cheng et al. "Subcritical water extraction of natural products". In: *Molecules* 26.13 (2021), p. 4004.

[23] Nuno Galamba et al. "Solubility of polar and nonpolar aromatic molecules in subcritical water: the role of the dielectric constant". In: *Journal of Chemical Theory and Computation* 15.11 (2019), pp. 6277–6293.

[24] Matthijs Justin Boel et al. "Hydrothermal liquefaction of plastics: a survey of the effect of reaction conditions on the reaction efficiency". In: *Reaction Chemistry & Engineering* 9.5 (2024), pp. 1014–1031.

[25] Juliano Souza dos Passos, Marianne Glasius, and Patrick Biller. "Screening of common synthetic polymers for depolymerization by subcritical hydrothermal liquefaction". In: *Process Safety and Environmental Protection* 139 (2020), pp. 371–379.

[26] Ziyue Dai et al. "Effect of diaminotoluene on the decomposition of polyurethane foam waste in superheated water". In: *Polymer Degradation and Stability* 76.2 (2002), pp. 179–184.

[27] Georgina C Laredo, Joel Reza, and Edith Meneses Ruiz. "Hydrothermal liquefaction processes for plastics recycling: A review". In: *Cleaner Chemical Engineering* 5 (2023), p. 100094.

[28] Reem Obeid et al. "A kinetic model for the hydrothermal liquefaction of microalgae, sewage sludge and pine wood with product characterisation of renewable crude". In: *Chemical Engineering Journal* 428 (2022), p. 131228.

[29] Luis Cutz et al. "Hydrothermal liquefaction of Elaeis guineensis trunks: Lessons learned from a case study in Guatemala". In: *Industrial Crops and Products* 206 (2023), p. 117552.

[30] Luis Cutz et al. "Hydrothermal liquefaction of Spanish crude olive pomace for biofuel and biochar production". In: *Journal of Analytical and Applied Pyrolysis* 188 (2025), p. 107050.

[31] Hui Jin et al. "Hydrothermal liquefaction of polycarbonate (PC) plastics in sub-/supercritical water and reaction pathway exploration". In: *ACS Sustainable Chemistry & Engineering* 8.18 (2020), pp. 7039–7050.

[32] Maja Čolnik et al. "Hydrothermal decomposition of polyethylene waste to hydrocarbons rich oil". In: *The Journal of Supercritical Fluids* 169 (2021), p. 105136.

[33] Bin Bai et al. "Experimental investigation on liquefaction of plastic waste to oil in supercritical water". In: *Waste management* 89 (2019), pp. 247–253.

[34] Department of Climate Change, Energy, the Environment and Water (DCCEEW). *Ethylbenzene. National Pollutant Inventory — Substance fact sheet*. National Pollutant Inventory. June 30, 2022. URL: `https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/ethylbenzene` (visited on 09/08/2025).

[35] Lab Pro Inc. *What is Toluene and Top 6 Uses*. URL: `https://labproinc.com/blogs/chemicals-and-solvents/top-5-uses-for-toluene` (visited on 09/08/2025).

[36] Noboru Yamazaki et al. “A linear trimer of p-isopropenyl phenol, a process for the preparation of the trimer, epoxy resins cured using the trimer and an epoxy derivative of the trimer”. European patent application EP0002887A1. Mitsui Toatsu Chemicals Inc. Application No. EP78300662; priority 1977-11-26. July 11, 1979. URL: `https://patents.google.com/patent/EP0002887A1/en` (visited on 09/08/2025).

[37] Cecilia Mattsson et al. “Chemical recycling of End-of-Life wind turbine blades by solvolysis/HTL”. In: *IOP conference series: materials science and engineering*. Vol. 942. 1. IOP Publishing. 2020, p. 012013.

[38] Špela Ferjan et al. “Sustainability assessment of the end-of-life technologies for biocomposite waste in the aviation industry”. In: *Polymers* 15.12 (2023), p. 2689.

[39] Jin Zhang et al. “Current status of carbon fibre and carbon fibre composites recycling”. In: *Composites Part B: Engineering* 193 (2020), p. 108053.

[40] Wolfgang Kandioller et al. “Elemental analysis: an important purity control but prone to manipulations”. In: *Inorganic chemistry frontiers* 9.3 (2022), pp. 412–416.

[41] *UNICUBE. Operating Manual*. Operating manual. Identification number 05 005 246. Elementar Analysensysteme GmbH. Langenselbold, Germany, Oct. 25, 2021.

[42] Solène Guggari et al. “Vanillin-based epoxy vitrimers: looking at the cystamine hardener from a different perspective”. In: *ACS Sustainable Chemistry & Engineering* 11.15 (2023), pp. 6021–6031.

[43] Yinghao Wang et al. “Analytical strategies for chemical characterization of bio-oil”. In: *Journal of separation science* 43.1 (2020), pp. 360–371.

[44] Lu Yuzhen et al. “Characterization of rapeseed oil using FTIR-ATR spectroscopy”. In: *J. Food Sci. Eng* 4 (2014), pp. 244–249.

[45] Mauro Mecozzi et al. “Monitoring of marine mucilage formation in Italian seas investigated by infrared spectroscopy and independent component analysis”. In: *Environmental monitoring and assessment* 184.10 (2012), pp. 6025–6036.

[46] Asep Bayu Dan Nandiyanto, Rosi Oktiani, and Risti Ragadhita. “How to read and interpret FTIR spectroscope of organic material”. In: *Indonesian Journal of Science and Technology* 4.1 (2019), pp. 97–118.

[47] *MAWL Calibration Worksheet. Maximum Allowable Water Loading calculation sheet*. PDF document. Technical worksheet. Document filename: ”MAWL Cal.pdf”; author/organization not specified. Feb. 20, 2025.

[48] Parr Instrument Company. *Series 4560 Mini Reactors, 100–600 mL. Specifications*. URL: `https://www.parrinst.com/products/stirred-reactors/series-4560-100-600-ml-mini-reactors/specifications/` (visited on 09/11/2025).

[49] Elementar Analysensysteme GmbH. *UNICUBE®. Organic elemental analyzer*. URL: `https://www.elementar.com/en/products/organic-elemental-analyzers/unicube` (visited on 09/13/2025).

[50] SPECTRO Analytical Instruments. *The Principle of ICP-OES*. URL: `https://www.spectro.com/icp-oes-principle` (visited on 09/10/2025).

[51] *SDT Q600. Simultaneous TGA/DSC — Specifications*. Product brochure. Document code L90010.001; © 2010 TA Instruments. New Castle, DE, USA, Jan. 18, 2011.

[52] Thermo Fisher Scientific. *Thermo Scientific Nicolet iS50 FTIR Spectrometer. Product Specifications*. Specification sheet PS52301$_E$. © 2020 Thermo Fisher Scientific. Oct. 2020. URL: `https://assets.thermofisher.com/TFS-Assets/MSD/Specification-Sheets/PS52301-nicolet-is50-ftir-spectrometer.pdf` (visited on 09/10/2025).

[53] Vincent Schenk et al. “Exploring the Limits of High-T g Epoxy Vitrimers Produced through Resin-Transfer Molding”. In: *ACS Applied Materials & Interfaces* 15.39 (2023), pp. 46357–46367.

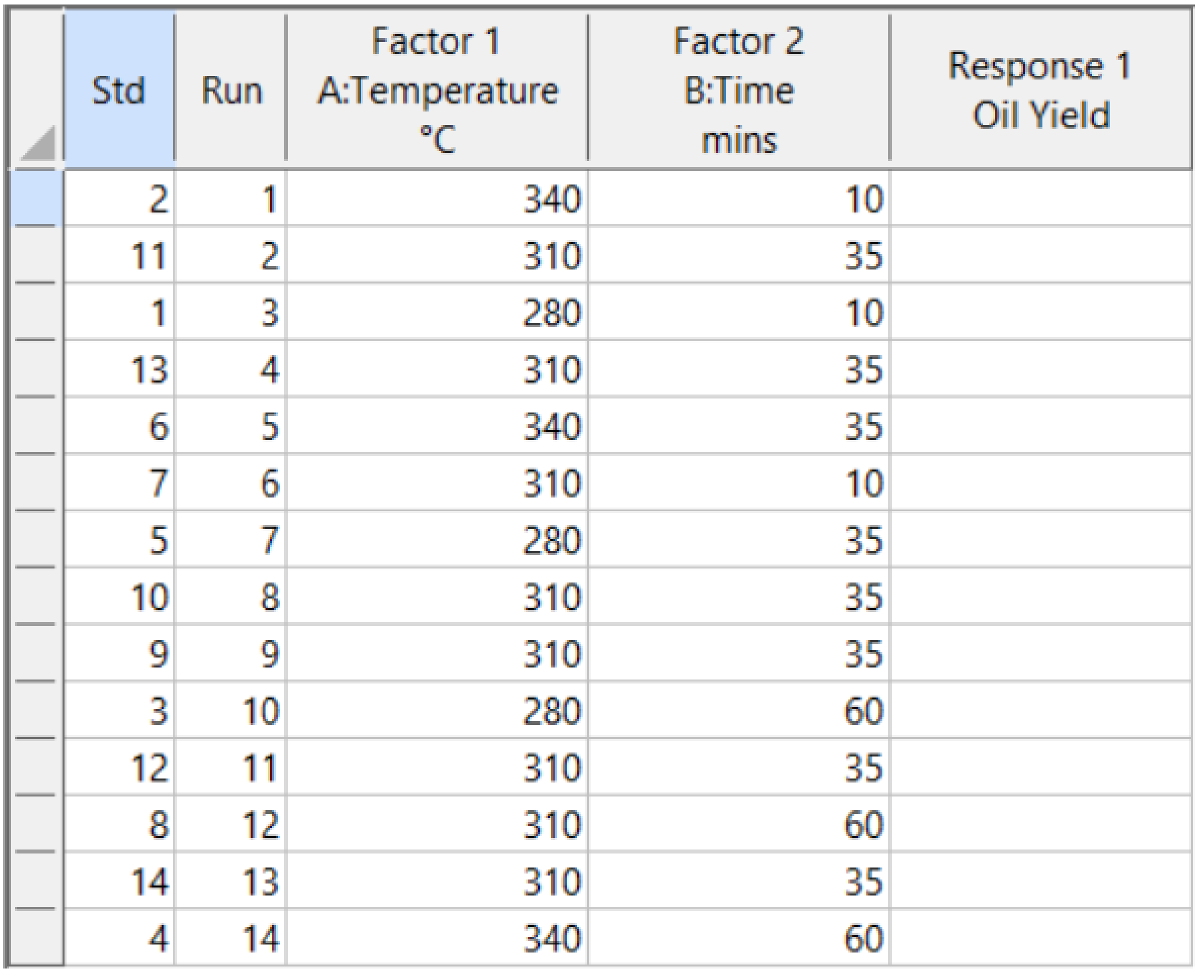
[54] André I Khuri and Siuli Mukhopadhyay. “Response surface methodology”. In: *Wiley interdisciplinary reviews: Computational statistics* 2.2 (2010), pp. 128–149.

A

Appendix

A.1. Design of Experiments (RSM)

The original Design of Experiments (DOE) which was not followed through is present here.



Std	Run	Factor 1 A:Temperature °C	Factor 2 B:Time mins	Response 1 Oil Yield
2	1	340	10	
11	2	310	35	
1	3	280	10	
13	4	310	35	
6	5	340	35	
7	6	310	10	
5	7	280	35	
10	8	310	35	
9	9	310	35	
3	10	280	60	
12	11	310	35	
8	12	310	60	
14	13	310	35	
4	14	340	60	

Figure A.1: DoE Image

A.2. Material Safety Data Sheet

A material safety data sheet was made for CFRP VR-RD composite. This had not been done before.

1-Page Safety Summary: Vitrimer Composite Lab Use

Scope. Quick reference for handling three materials used with the vitrimer system: **Vitrimer Composite (epoxy blend)**, **1-Thioglycerol**, and **Potassium Hydroxide (KOH) pellets**. Use alongside full SOPs/SDSs.

Top Hazards (by material)

- **Vitrimer Composite (epoxy blend):** Skin/eye irritant; delayed skin sensitizer; harmful to aquatic life (long-lasting). Combustible; toxic fumes on burning.
- **1-Thioglycerol:** Toxic by inhalation/skin/ingestion; strong eye/skin irritant; severe aquatic hazard. Toxic sulfurous fumes when heated.
- **Potassium Hydroxide (KOH) pellets:** Strong base—causes severe burns to skin/eyes; corrosive if swallowed; dust irritant to respiratory tract; hygroscopic; reacts with acids/metals; corrosive fumes in fire.

Required Controls & PPE

- **Work area:** Fume hood or LEV; prevent aerosol/vapour/dust formation; keep away from drains.
- **Minimum PPE:** Safety goggles, lab coat, chemical-resistant gloves; for KOH and spills, add face shield and apron; respirator if airborne risk.
- **Environmental:** Never discharge to sinks; collect wastes/contaminants in labelled containers.

Safe Handling & Storage

- **Vitrimer Composite:** Avoid skin contact; store cool, dry, ventilated; away from oxidisers; use epoxy-compatible containers.
- **1-Thioglycerol:** Handle in hood; minimize vapour; store tightly closed in a cool, ventilated, locked cabinet.
- **KOH pellets:** Keep dry in original, corrosion-resistant container (15–25 °C); protect from moisture; segregate from acids/aluminium/metals.

First-Aid (immediate actions)

- **Inhalation:** Move to fresh air; monitor breathing; seek medical attention (urgent for thioglycerol).
- **Skin:** Remove contaminated clothing; rinse/shower $\geq$15 min; urgent care for KOH; monitor epoxy sensitization.
- **Eyes:** Irrigate continuously $\geq$15 min; remove lenses; urgent ophthalmology for KOH/thioglycerol.
- **Ingestion:** Rinse mouth; *do not* induce vomiting; small water if conscious; call poison centre immediately (KOH/thioglycerol).

Spill, Leak, and Fire Response

- **Small spills:** Absorb with inert material (sand/vermiculite), place in sealed container; wash area with detergent (thioglycerol); prevent drain entry. For KOH, carefully sweep or dissolve then **neutralize with dilute acid**; retain wash water.
- **Fire-fighting:** Water spray, foam, CO_2, or dry powder as appropriate; expect toxic/irritant oxides/-fumes; use SCBA and full protective gear. (KOH is non-combustible but emits corrosive oxides in fire.)

Waste & Decontamination

- Collect epoxy/thioglycerol residues as hazardous organic waste; segregate strong base (KOH) waste and neutralize per local rules; label all containers; document disposal.

Quick Decision Guide

- **Burn/eye splash?** Flush ≥15 min → urgent medical attention.
- **Skin rash after epoxy?** Stop exposure; seek medical advice—possible sensitization.
- **Unknown exposure?** Treat conservatively; call supervisor and safety officer; consult SDS.

A.3. Nuclear Magnetic Resonance

A quick Nuclear Magnetic Resonance (NMR) analysis was conducted only for 340-60-CRUDE. Presence of aniline, albeit impure, was detected.

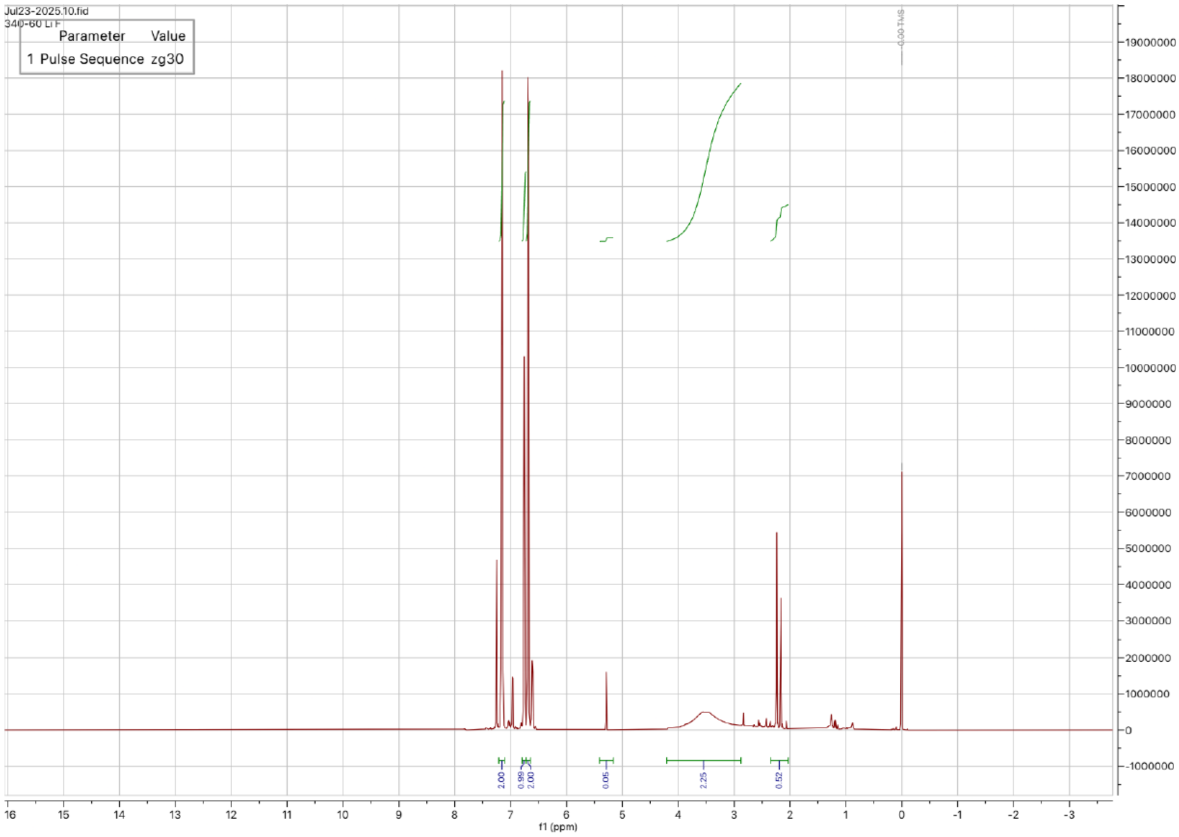


Figure A.2: NMR-340-60 CRUDE