

**CONTROLLED AUTOXIDATION OF HEAVY PETROLEUM
FOR CARBON FIBER PRECURSORS**

BY

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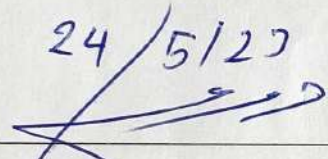
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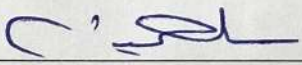
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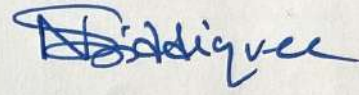
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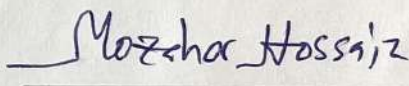
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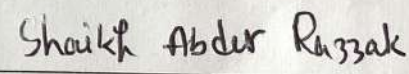

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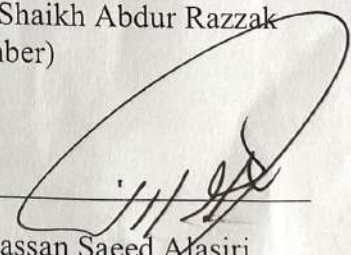
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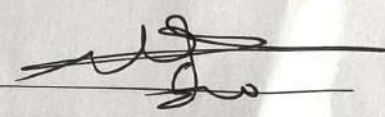



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*This thesis is dedicated to both my
late father and eldest daughter:
Said Mohamed and Saadiya Lahmady.
may their souls continue resting in Jannah.*

PREFACE

The present preface serves to inform the reader of the forthcoming publication of two articles from this thesis in the esteemed peer reviewed journals, Chemical Engineering Journal, published by Elsevier and The Chemical Record, published by Wiley. One has been submitted for publishing in Chemical Engineering Journal entitled "*Controlled Autoxidation of Heavy Vacuum Gas Oil (HVGO) to Produce Carbon Fiber Precursors*" while the second will be published in The Chemical Record under the title "*Prospect and Challenges of Carbon Fibre Production from Heavy Petroleum*", and lastly a US Patent has been submitted under the title "*Controlled Autoxidation of Heavy Vacuum Gas Oil (HVGO) toward High-Value Carbon Fibers*".

The first author of these chapters, Lahmady S. Mohamed, assumes responsibility for the conceptualization of the research, the collection and analysis of the data, and the composition of the manuscript. Additionally, the supervisory authors, Dr. Muhammad N. Siddiquee and Prof. M. Mozahar Hossain, provided valuable contributions to the conceptualization of the research, the analysis of the data, and the composition of the manuscript.

It is worth noting that the research presented in these chapters contributes to the current knowledge and understanding of the production of carbon fiber precursors through the autoxidation of heavy petroleum. These chapters would serve as an important reference for further research in this field.

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I humbly and gratefully give all praise to Allah, the Omnipotent, and the Sustainer, and pray that His divine blessings be upon the last and final prophet, Prophet Muhammad (PBUH), his family, and close companions until the Day of Judgment. Ameen.

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My mother has always been my rock and a constant source of inspiration, and for that, I am deeply grateful. I cannot thank my siblings enough for always being there for me as well. My lovely wife, two daughters, and son have been my biggest motivation and source of joy, and I am forever grateful for their love, laughter, understanding, and support which have been a constant source of light in my life. Without them, I could not have achieved what I have today, and I am forever thankful.

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LIST OF ABBREVIATIONS

B.P.	:	Boiling Point
CNMs	:	Carbon Nano-Materials
CTP	:	Coal Tar Pitch
DSC	:	Differential Scanning Calorimeter
FCC	:	Fluid Catalytic Cracking
FT-IR	:	Fourier Transform Infrared
GPCF	:	General Purpose Carbon Fibers
HPCF	:	High Performance Carbon Fibers
HT-VGO	:	Hydrotreated Vacuum Gas Oil
HVGO	:	Heavy Vacuum Gas Oil
LAMMPS	:	Large-scale Atomic/Molecular Massively Parallel Simulator
LLDPE	:	Linear Low-Density Polyethylene
MOS	:	Metal Oxide Semiconductor
MS	:	Mass Spectrometry
NMR	:	Nuclear Magnetic Resonance
SIMDIST	:	Simulated Distillation
TGA	:	Thermogravimetric Analysis
UV-Vis	:	Ultraviolet-Visible
VGO	:	Vacuum Gas Oil

ABSTRACT

Full Name : Lahmady Said Mohamed
Thesis Title : Controlled Autoxidation of Heavy Petroleum for Carbon Fiber Precursors
Major Field : Chemical Engineering
Date of Degree : May 2023

Carbon fiber is an ultra-light strong material that is very promising for aviation, automobiles, military, and sports. Its market size in 2022 was USD 6.5 billion and is expected to increase to USD 21.7 billion in 2032. However, traditional polyacrylonitrile (PAN)-based carbon fiber (CF) is expensive due to higher raw material and processing costs that limit the extensive production and use of CF. The objective of the current research was to develop a sustainable, cheap, and efficient pre-treatment method to produce CF precursors from heavy petroleum following controlled autoxidation (oxidation with air). Different heavy petroleum fractions, including vacuum gas oil (VGO), heavy vacuum gas oil (HVGO), and hydro-treated vacuum gas oil (HT-VGO) were used as carbon sources in a semi-batch process where feed was batch and gas was continuous. The experiments and analyses were conducted to investigate the effects of temperature (130–260 °C), time (4–48 hours), oxygen partial pressure (N_2 /air), and mixing. An increment was observed in viscosity (from 729 cP to 1979 cP), aromaticity (37% reduction in aliphatic H), cross-linking, and softening point (from 37.2 °C to over 200 °C), while volatility decreased due to the free radical addition (heavier) product formation, removal of lower boiling fractions, and ring closure, and treated hydrocarbon fractions can be used as a CF precursor. Besides, experiment performed at elevated temperatures and time by blowing N_2 /air without mixing

had showed better desired properties compared to those in rigorous mixing at lower duration and temperature. Additionally, heating in the presence of nitrogen for some operating conditions produced more effective precursors than in the presence of air. Overall, it was concluded that this controlled autoxidation study would lead to developing an alternative, cheap and sustainable way to produce CF precursor from the low-value heavy petroleum fractions.

Keywords: Carbon Fiber, Autoxidation, Heavy petroleum fractions, Softening Point, Precursor.

ملخص الرسالة

الاسم الكامل: لعمدي سعيد محمد

عنوان الرسالة: الأكسدة الذاتية المتحكممة للبترول الثقيل لإنتاج مواد سابقة للألياف الكربونية

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: مايو 2023

ألياف الكربون هي مادة قوية وخفيفة للغاية واعدة جدًا للطيران والسيارات والجيش والرياضة. بلغ حجم سوق الياف الكربون في عام 2019 4.7 مليار دولار أمريكي ومن المتوقع أن يرتفع إلى 13.3 مليار دولار أمريكي في عام 2029. ومع ذلك، فإن ألياف الكربون التقليدية القائمة على البولي أكريلونيتريل (PAN) باهظة الثمن بسبب ارتفاع تكاليف المواد الخام والمعالجة التي تحد من الإنتاج المكثف واستخدام التلبيف الكيسي. كان الهدف من البحث الحالي هو تطوير طريقة معالجة مسبقة مستدامة ورخيصة وفعالة لإنتاج سلائف ما قبل CF من البترول الثقيل بعد الأكسدة التلقائية الخاضعة للرقابة (الأكسدة بالهواء). تم استخدام المشتقات بترولية ثقيلة مختلفة، بما في ذلك زيت الغاز الخوائي (VGO) وزيت الغاز الثقيل (HVGO) وزيت الغاز الخوائي المعالج بالهيدروجين (HT-VGO) كمصادر للكربون في عملية نصف دفعية حيث تم التغذية بالدفعات والغاز كان مستمرًا. أجريت التجارب والتحليلات لبحث تأثيرات درجة الحرارة (130-260 درجة مئوية) والوقت (4-48 ساعة) والضغط الجزئي للأكسجين (N_2 / الهواء) والخلط. لوحظت زيادة في اللزوجة (من ~ 729 سنتي بواز إلى حوالي 1979 سنتي بواز)، العطرية (انخفاض بنسبة 37 % في الأليفاتية H)، والربط المتبادل، ونقطة التليين (من 37.2 درجة مئوية إلى أكثر من 200 درجة مئوية)، بينما انخفض التقلب بسبب إلى إضافة الجذور الحرة (الأثقل) إلى تكوين المنتج، يمكن استخدام إزالة المشتقات المنخفضة الغليان، وإغلاق الحلقة، المشتقات الهيدروكربونات المعالجة كسلائف ما قبل CF. إلى جانب ذلك، فإن الأكسدة التلقائية في درجات حرارة ووقت مرتفعين عن طريق نفخ N_2 / هواء بدون خلط كانت لها قيم خواص أعلى من تلك الموجودة في الخلط الصارم بمدة ودرجة حرارة أقل. بالإضافة إلى ذلك، فإن التسخين بوجود النيتروجين في بعض ظروف التشغيل أنتج سلائف أكثر فعالية من وجود الهواء. بشكل عام، تم اكتشاف أن هذه الدراسة ستؤدي إلى تطوير طريقة بديلة ورخيصة ومستدامة لإنتاج سلائف ما قبل CF من المشتقات البترولية الثقيلة منخفضة القيمة.

الكلمات الرئيسية: ألياف الكربون، الأكسدة الذاتية، كسور البترول الثقيل، نقطة التليين، مادة سابقة.

CHAPTER 1

INTRODUCTION

In recent years, the never-ending increase in global energy demand caused by market expansion and massive population shift has resulted in a reduction in petroleum reserves, which has been characterized by increased production efficiency and refining (Santos & Lo, 2014). The global consumption of petroleum and other liquid fuels increased from 90 million barrels per day (MBPD) in 2010 to 100 MBPD in 2020 and is predicted to be 121 MBPD in 2040 due to an increase in demand (Alawad & Al Zubaidi, 2019; Lucintel, 2022). Now as an outcome, there is indeed a massive disparity in the world's energy supply, which has global economic ramifications. The capacity of the petroleum industry to transform possibilities into a nation's monetary reserves is required to fill this gap (Lucintel, 2022; Market Research Report, 2023).

The upgrading of heavy and extra-heavy oil seems to be an indispensable ingredient in today's petrochemical industry. Petroleum refiners have been trying to discover alternative opportunities across several upgrading processes to efficiently utilize heavy and extra hydrocarbons (Sawarkar, 2019). Currently, conventional crude oils supply most of the energy. Substantial research is being conducted to find alternative sources of energy; however, progress is still in its preliminary phase to meet the increasing energy requirements. To meet these needs, low-value unconventional oil feedstocks such as oilsands bitumen, shale oil, heavy oil, and vacuum residue are being used. Heavy petroleum fractions have been obtained from both conventional and unconventional source materials,

and it is hard to produce value-added fuels from the heaviest naphtha (Alcaniz-Monge et al., 1997; Kim et al., 2021; Park, 2015).

Recovery, transportation, processing, and storing difficulties of heavy petroleum fractions are all known challenges (Saniere et al., 2004). Alternative products with added value from the heavy petroleum fraction are highly desirable. There has been an increase in demand for Carbon Fibers (CFs) (Figure 1) for the fulfillment and diversification of the production of wind current generator blad, a new inception of automobile fuel tanks, the carbon fixtures in construction materials, and the production of construction elements for structures is undergoing a turbulent development in hydrogen energies for more than 20 years. CFs are currently in high demand in the aerospace and defense industries, as well as in sporting goods (Jana et al., 2022; Lucintel, 2022; Market Research Report, 2023).

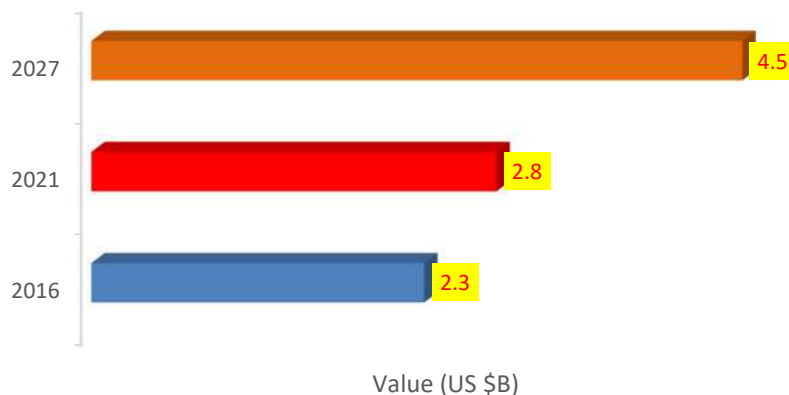


Figure 1 Trends and forecasts for the global CF market (US \$B)

(Lucintel, 2022)

The widespread profitable use of CFs is hampered by their exorbitant cost, which varies primarily with the type of carbon feedstock. Typical CF manufacturing procedures make use of expensive raw materials such as hydrocarbons and graphite (Barr & Lewis,

1978). Precursor budget consumes more than half of the total cost for CFs production; therefore, embracing low-cost CF precursors has been exploited as one of the major approaches to developing cheap CFs. A possible solution to the problems mentioned above is to design intricate composite forms based on C-CFs, which would not only improve the properties of fibers but would also significantly reduce their cost (Chacón-Patiño et al., 2023; Radjef et al., 2021).

The incorporation of certain chemicals is not economically viable in the production of carbon fibers and must be recovered/removed prior to the next steps, which is extremely difficult due to the extremely high viscosity of the condensed hydrocarbons. Controlled autoxidation (air oxidation) can, however, be used to improve the softening points of heavy petroleum residue (Alcaniz-Monge et al., 1997). Despite extensive heavy oil disposal, the documented annual fabrication in 2000 accounted for only 12% of total annual manufacture. Furthermore, heavy oils of higher quality in terms of composition and density are given priority in fuel production (Santos & Lo, 2014).

The raw materials for CF production have been predominantly focused on polyacrylonitrile (PAN), mesophase, and coal tar pitch (CTP) based heavy petroleum. In this study, the focus has been shifted to a specific reaction of autoxidizing heavy petroleum cuts. Autoxidation is defined as a conversion pathway that has the potential to add value to low-value multinuclear aromatic-rich coal liquids, heavy oils, and bitumen (Montoya Sánchez & de Klerk, 2018). The autoxidation chemistry used in this research was by the passage of air (utilizing the ~21% oxygen) by either bubbling into the heated reactants or blowing over it.

Since pitch-based precursors show an 85% yield then further examination is presently being conducted on selected heavy petroleum such as HVGO. This study looks at heavy petroleum fraction which was pre-treated following controlled free radical oxidation chemistry to impart the properties so that it can be used as carbon fiber precursor. The effects of temperature, time, and mass transfer were investigated. Experiments were carried out at temperatures ranging from 130 °C to about 260 °C for varying periods in the presence of air/nitrogen gas. Because of the free radical addition (heavier) product formation, removal of lower boiling fractions, and ring closure, it was expected that molecular weight, aromaticity, cross-linking, and the softening point would increase.

1.1 Research Objectives

The main goal of the current study was to develop a sustainable, cheap, and efficient pre-treatment method to produce carbon fiber precursors from heavy petroleum fractions following controlled autoxidation (oxidation with air). The specific goals were:

- i. To investigate the thermal effect of producing carbon fiber precursors from heavy petroleum cuts. The heavy petroleum's low boiling fraction would be eliminated, and structural rearrangement would occur to form a heavier product. Because of the availability of the persistent free radical in heavy petroleum product would also form.
- ii. To comprehend the role of oxygen partial pressure in the formation of heavy products following the free radical path. More free radicals are expected to form at higher oxygen pressures, facilitating the formation of addition products, but

this increases the possibility of oxygen incorporation in heavy petroleum, which is not beneficial as a carbon fiber precursor. The partial pressure of oxygen was controlled by supplying different levels of oxygen.

- iii. To assess the role of mixing and gas-liquid interfacial per unit liquid volume in the formation of additional products. It is expected that increasing the gas-liquid interfacial area would facilitate free radical formation while decreasing mixing would increase addition product formation.
- iv. To characterize the controlled autoxidation products to determine their suitability as a carbon fiber precursor. Heavier product formation was anticipated to increase the molecular weight distribution of petroleum fractions, cross-linking, and aromaticity, resulting in higher softening points and hardness.

The successful completion of the research would allow for the production of carbon fiber precursors from low-value heavy petroleum fractions using air, a cheap, readily available, and industrially oxidizing agent. Furthermore, this study would lay the groundwork for future research on carbon fiber manufacturing, as well as asphalt/bitumen hardening, weathering, fouling, storage stability, and sludge formation.

1.2 Research Novelty

To the best of the author's knowledge, the scope of the proposed work herein does not overlap with current or previous research around the institution. Even in the literature, there is little effort to pre-treat heavy petroleum to produce carbon fiber

precursors. The majority of the research focuses on chemical treatments such as bromine (Y. O. Choi & Yang, 2001a) or when working with coal tar pitch (Alcaniz-Monge et al., 1997; Barr & Lewis, 1978). Heavy petroleum was pre-treated in the current study to modify its properties by manipulating oxygen availability and free radical formation.

Significant work has also been done to fundamentally understand the reaction mechanism that forms heavy products, the compound class responsible for heavy product formation, and how to prevent the formation of addition (heavy) products. However, heavy product formation has applications, such as the current research to improve the softening point of petroleum-based carbon fiber precursors. Previously, just air was used as an oxidizing agent in the bitumen oxidation process to yield oxidized products with oxygen—containing functional groups.

The current study aims to control product formation to reduce oxygen functional groups and increase addition (heavy) product formation. There is evidence that the rate of additional radical formation is affected by the gas-liquid interface, but selectivity to addition products within oxygen incorporation is affected by oxygen availability and liquid phase mixing (Siddiquee et al., 2018, 2020). This study would be an excellent testbed for determining whether these are correct and whether a process could be designed to capitalize on these fundamental insights. The heavy resulting product by controlled autoxidation did have a higher boiling point ranges, cross-linking, aromaticity, and softening point, which are critical attributes of carbon fiber precursors.

1.3 Scope and Outline of the Work

The controlled autoxidation of heavy petroleum to produce carbon fibers is a complex chemical process that requires a high degree of technical expertise and specialized equipment. The success of this process depends on the quality of the heavy petroleum feedstock, the efficiency of the autoxidation process, and the quality control measures that are in place during the CF production process. In the current study, the scope of work for the controlled autoxidation of heavy petroleum to produce carbon fibers and to achieve the goals are as follows:

- i. Thermal and time effect, and role of oxygen partial pressure in producing carbon fiber precursors were studied by using heavy petroleum cuts-VGO, HT-VGO, and mainly HVGO maintaining operating conditions of temperature range 130 – 260 °C and time 4 – 48 hours in the presence of air and nitrogen. In both cases air (or nitrogen) was introduced by bubbling and a stirring bar was used to facilitate the mixing. The experiment performed in the presence of nitrogen was considered as a controlled experiment and would exhibit purely thermal effect. The autoxidation performed (in the presence of air) would depict the effect of thermal and oxygen partial pressure.
- ii. The role of mixing and gas-liquid interfacial per unit liquid volume were also studied by using HVGO maintaining operating conditions of temperature range 130 – 260 °C and time of 4 – 48 hours in the presence of air and nitrogen, but only blowing air (or nitrogen) without any bubbling and any mixing by a magnetic stirrer.

- iii. The suitability of the heavy petroleum precursors for use in CF production was evaluated based on certain physical and chemical properties. The parameters examined include boiling point ranges, aromaticity, molecular weight, viscosity, thermal stability, and H/C aliphaticity and aromaticity. These properties are selectively analyzed, and their outcome has been elaborated in the study.

Chapter two briefly elaborated a literature review on the general topic of controlled autoxidation of heavy oils to produce carbon fiber precursors.

Chapter three reported on how the experiment was conducted by illustrating the main procedure of the study and subsequent methodologies of analysis.

Chapter four detailed the results and their interpretation based on scientific evidence and all new findings referenced accordingly.

Chapter five concluded this thesis and gave viable recommendations for future studies and examinations on the topic of interest.

CHAPTER 2

LITERATURE REVIEW

This chapter has reviewed the current state of research on three interconnected areas of materials science and engineering: petroleum fractions, autoxidation, and carbon fibers and their precursors. Petroleum fractions are known to be complex mixtures of hydrocarbons that are widely used as feedstocks to produce fuels, chemicals, and materials. The production and processing of these fractions involve various techniques such as distillation, cracking, and blending, which yield different types of fractions with varying properties and compositions (Altgelt & Boduzynski, 1994).

Among these fractions, heavy products such as vacuum gas oils and residues are of particular interest due to their high potential for conversion into value-added products such as carbon fibers. CF are high-strength, lightweight materials with a wide range of applications in aerospace, and automotive among other industries (Frank et al., 2012; Park, 2015).

However, the production of CF from heavy products requires a thorough understanding of the autoxidation chemistry involved in their formation, as this can lead to the formation of byproducts and the degradation of the materials. In this literature review, an examination of the current state of research on petroleum fractions, carbon fibers, and autoxidation chemistry, with a focus on the formation of heavy products and their conversion into carbon fibers has been provided. Therefore, in this chapter, a comprehensive overview has been elaborated of the existing literature on these three areas,

highlighting key findings and knowledge gaps, and discussing the implications of these findings for future research and practical applications.

2.1 Petroleum Fractions

Petroleum is a complex mixture of hydrocarbons among other hetero-atom elements such as nitrogen, oxygen and sulfur which vary not only in amounts but leads to variability in viscosity, volatility and specific gravity. Due to these various concentrations, petroleum's physical properties and color vary hugely from oil well to another on different regions (James G. Speight, 2014). During the refining process, crude oil is heated and separated into various fractions based on their boiling points. The following are the main fractions of petroleum: Gasoline, Naphtha, Kerosene, Diesel, Gas oil, and Residuals. The latter fraction has a boiling range above 400 °C and contains heavy hydrocarbons and other impurities whereby it is used as a feedstock for the production of asphalt, and fuel oil among others (Alawad & Al Zubaidi, 2019; James G. Speight, 2014; Li et al., 2018).

Each petroleum fraction's specific boiling range and properties depend on the crude oil source and the refining process used. These fractions are further processed and refined into various products, including fuels, lubricants, solvents, and petrochemicals. Now to comprehend the genesis of CF production from its raw materials, this section endeavor to highlight some of the vital background on petroleum fractions that play a key role in the carbon fiber spectra (James G. Speight, 2014; Rodgers & McKenna, 2011).

There are two types of oils classified based on certain factors. Some scientists have conducted this by classifying either conventional or non-conventional oils. Unconventional

oil has piqued the interest of refiners as a source of alternative energy. Heavy crude oil is divided into several categories, including heavy oils, extra heavy oil, oil soil, tar sands, oil shale, and bitumen, all of which are unconventional oil resources. Such oils have a high concentration of high molecular weight hydrocarbons as well as a high concentration of hetero compounds like sulfur, nitrogen, oxygen, and metals. Oil companies and organizations typically use oil inference criteria that take into account both their financial position and the level of technological advancement. (Rodgers & McKenna, 2011; Santos & Lo, 2014).

According to recent studies, unconventional oil reserves, exceed 6 trillion barrels. This equates to roughly 70% of the world's total energy resources derived from fossil fuels. There are approximately 135 Gbbl of heavy oils in the Middle East region alone (Castañeda et al., 2012; Saniere et al., 2004; Santos & Lo, 2014). Sulfur, nitrogen, oxygen, and heavy metals are common impurities in residue or heavy oil. These impurities have an impact on the oil's properties and product quality. The level of these impurities, however, is determined by the crude's origin (Alawad & Al Zubaidi, 2019).

2.2 Background of Carbon Fibers

In the last 20 years, the demand for carbon fibers (CF) has been increasing by about 12% yearly, mostly in the progress of lightweight automotive components (Z. Hui Yang et al., 2019). The forecasted growth of CF fabrication and utilization is typically correlated with the US program for producing new aircraft by Boeing (specifically, the Boeing 777

and 7E7 Dreamliner), and in Europe, with the escalation in consumption of carbon-fibre-reinforced plastics by Airbus (Lysenko, 2007).

Moreover, there has been increased order for CF fulfillment and diversification of production of blades for wind current generators, a new inception of fuel tanks for automobiles, usage of carbon fixtures in building materials, and the turbulent development of production of construction elements for structures in hydrogen energies (Lysenko, 2007). Presently, CF has a massive demand in the aerospace and defense sectors for sporting items, automotive industry and wind energy applications. It has been noted that, there exist potential fields like medical devices, robotics and civil needs (Banerjee et al., 2021).

Joseph Swan invented carbon fibers (CFs) in 1860, when he filed a patent for the use of a light bulb filament. Biomaterials such as cotton and bamboo were initially used as precursors. (D. Choi et al., 2019). Carbon fiber is a thin (diameter: 5-10 micrometers), mostly carbon-atom-based material that is light but strong (Bhatt & Goe, 2017; Hiremath et al., 2017). Because of its high strength and modulus, it is increasingly used as a reinforcing material. It has a wide range of applications in industries such as automotive, aviation, civil engineering, military, and sports, and there are numerous other sectors where carbon fiber could potentially be used (Bhatt & Goe, 2017; Y. O. Choi & Yang, 2001a; Newcomb, 2016). CFs are gaining popularity due to their chemical properties, high electrical conductivity, and mechanical strength, which make them promising structural materials for aforementioned various industries (Daulbayev et al., 2021; Park, 2015).

2.2.1. Types of Carbon Fibers and their Raw Materials

To produce carbon fibers, many various sorts of precursors have already been explored. CF precursors should have easy conversion to CF, a high carbon yield, and low processing costs. The four categories of precursors outlined below have been extensively utilized and have been substantiated to be the most successful in this regard (Park, 2015). Carbon fiber precursors include coal, petroleum, or plant-based pitches, along with polyacrylonitrile (PAN) (Leistenschneider et al., 2021; Park, 2015):

1. Acrylic precursors- most industrial manufacturers have been successfully using them for carbon fiber preparation for quite some time now. More than 85% of the monomer in these acrylic precursors is acrylonitrile (AN). PAN is the most commonly used acrylic precursor in the production of carbon fibers. An example of such an oxidation reaction pathway is shown in Figure 2. The figure highlights how the initial raw material is first dehydrogenated and cyclized, repeatedly, to form cyclic rings. Thereafter, oxidized accordingly and the smaller fractions combine to form a long cyclic chain of organic product which when specially carbonized, ends up with a large, concrete cyclic addition product that is bigger structurally than its feed.

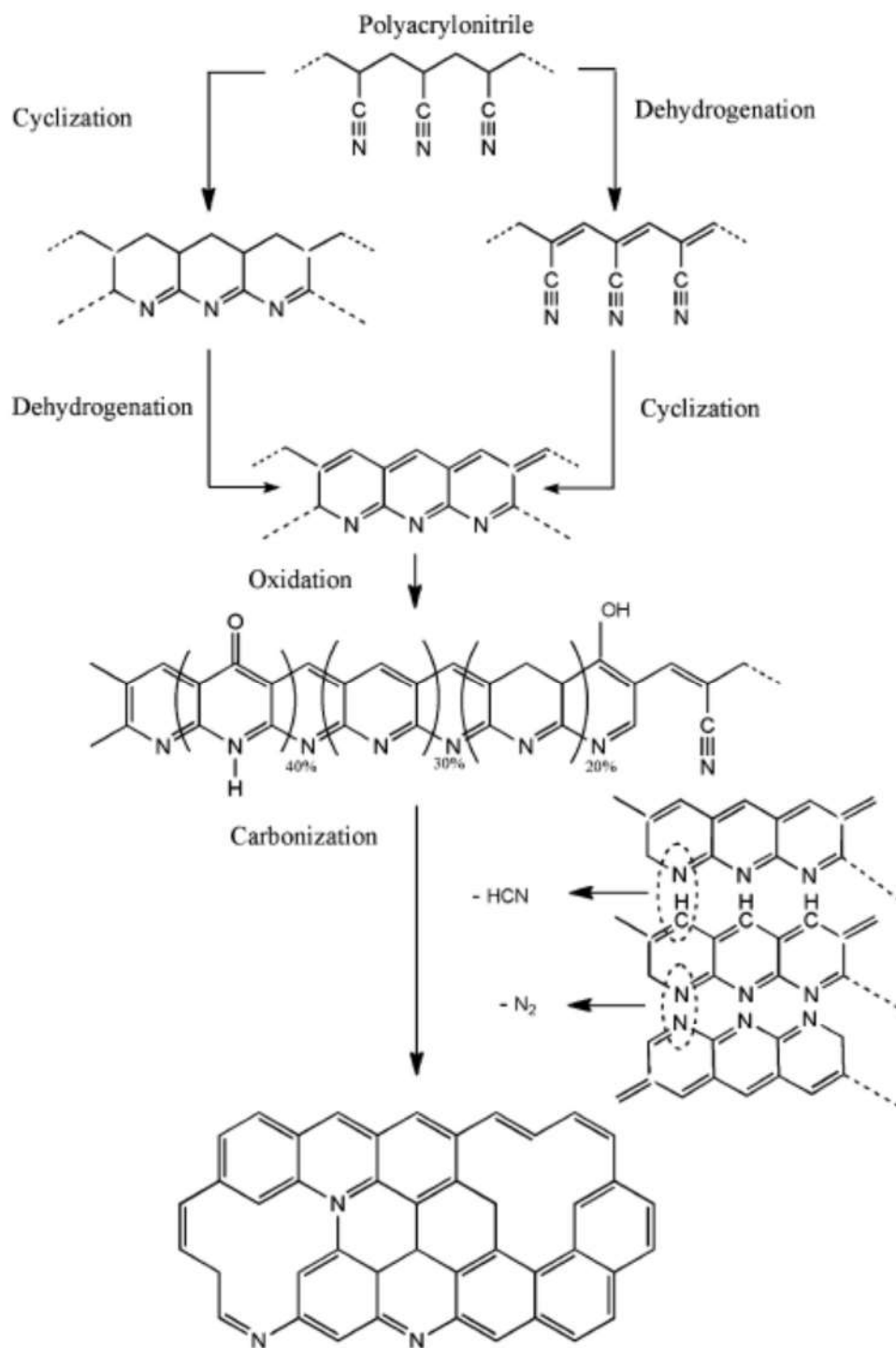


Figure 2 Typical reaction route for CF production from PAN

Reprinted with permission from (Frank et al., 2012)

2. Cellulosic precursors are made up of 44.4% carbon. Despite this, the reaction appears to be more complicated and challenging than simple dehydration, and the carbon total emissions are only about 25–30%.
3. Pitch-based precursors: They have an 85% yield and, due to their relatively high graphitic character, the subsequent carbon fibers have a high modulus. PAN-based carbon fibers have better compression and transverse characteristics than pitch-based carbon fibers.
4. Other types of carbon fiber precursors: Vinylidene chloride as well as phenolic resins have been investigated as carbon fiber precursors but still haven't been shown to be cost competitive.

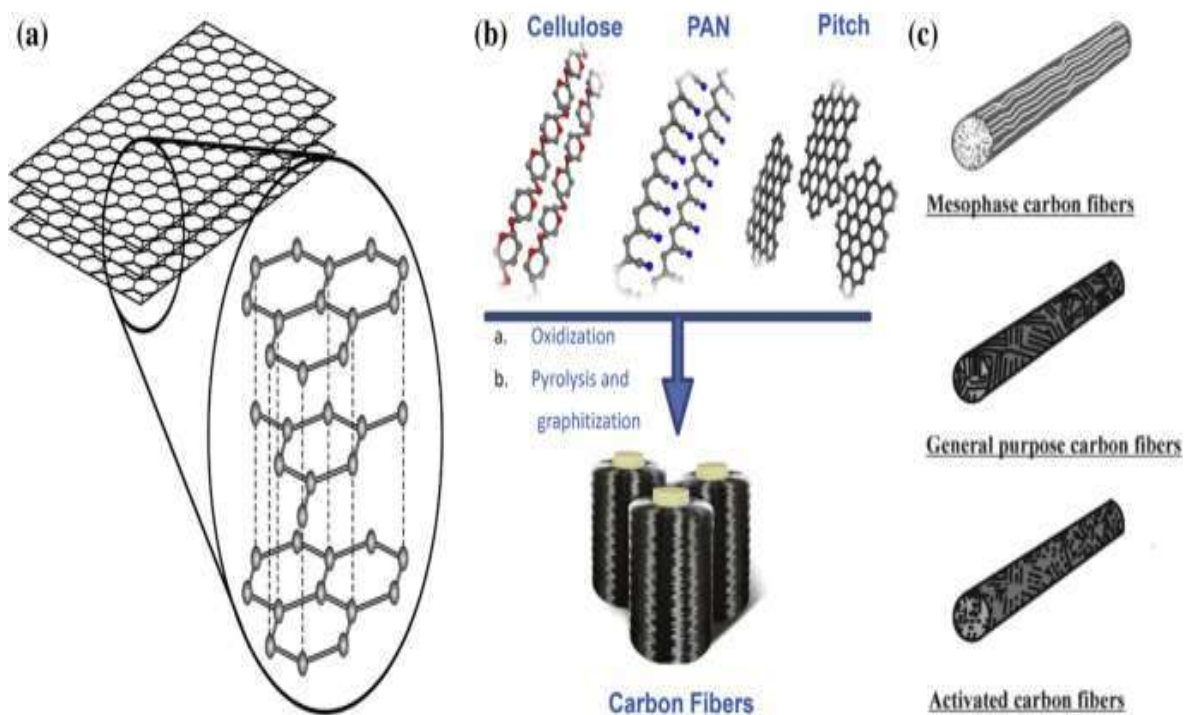


Figure 3 Schematic illustration of types, cross section, and precursors of CFs

(a) Close-up of an atomic structure of CF cross-section, (b) CF Precursors, (c) CF types
 Reprinted with permission from (Srivastava et al., 2020)

About 96% CF has conventionally been made of PAN and rayon. Whereby that pitch rayon-based CF production has already been reduced due to poor quality (Jana et al., 2022). PAN-based carbon fibers have excellent mechanical properties compared to pitch-based carbon fibers attributed to the prevalence of condensed polymeric aromatic structures, stacking, and cross linking. However, pitch-based CF has a significantly greater tensile modulus (D. Choi et al., 2019; Newcomb, 2016; Park, 2015).

PAN-based carbon fiber is costly to produce, and one viable solution is to yield raw materials for carbon fiber fabrication using heavy oil feedstock. Heavy hydrocarbon raw material is widely obtainable at a lower cost than PAN. Heavy petroleum has a high potential for production of CF, which is among the few significantly greater major multinational market products. The main challenges of producing CF from oil products are the relatively low softening points, structural variations, and compositional complexity of heavy petroleum. Conventional treatment efforts to develop CF precursors from heavy petroleum are scarce (Y. O. Choi & Yang, 2001; Leistenschneider et al., 2021).

The need to establish some reduced in cost CF manufacturing methods is a major driving force of studies in this field. CFs' commercial applications are presently hampered by their huge costs, which are principally determined by the category of carbon raw material used (Alcaniz-Monge et al., 1997). Carbon fiber manufacturing costs is a little less than \$10/kg for prevalent use in low-energy and ecological applications (J. Yang et al., 2016). A potential approach is by using the petroleum and coal tar pitch as a cheap raw feedstock to yield Carbon Nano Materials (CNMs) (Daulbayev et al., 2021). Coal tar pitch is the term used to describe the non-volatile residue of coal tar distillation that remains after

undergoing high-temperature pyrolysis exceeding 1000 °C and is characterized by its stability at temperatures as high as 450 °C (Bermudez et al., 2018).

The oil sector refers to many refined products from heavy oils as "pitch". This could cause significant debate and controversy outside of the refining general public. Pitches are sophisticated complex mixtures of polyaromatic molecules and heterocyclic substances that can comprise well over 80% carbon, and their content varies depending on the origin tar and processing parameters. Natural pitches are created through the refining of oil products and the destructive distillation of coal, whereas synthetic pitches are created through the pyrolysis of synthetic polymers (Park, 2015). The pitches used as starting materials for carbon fiber production are by-products of the coke and petrochemical industries. As a result, these materials have the advantage of being inexpensive carbon fiber precursors. Otani and colleagues created the first pitch-based carbon fibers in 1963. Based on pitch, two types of carbon fibers can be distinguished: general purpose carbon fibers (GPCF) and high-performance carbon fibers (HPCF) (Alcaniz-Monge et al., 1997; D. Choi et al., 2019).

Isotropic pitches are used to make GP pitch carbon fibers, which are not graphitic and have poorer properties than HP pitch carbon fibers, which require a special treatment process to convert the pitch to a mesophase grade, i.e., an optically anisotropic and graphitic material. Whereas mesophase pitches used in the production of high-modulus carbon fibers can be formed either through the thermal polymerization of petroleum- or coal-tar-based pitches or through the catalytic polymerization of pure compounds such as naphthalene (Jana et al., 2022; Maeda et al., 1993; Park, 2015).

2.2.1.1. Dissimilarities of Coal Tar and Petroleum Pitches

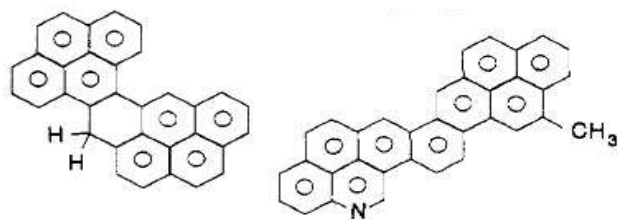
Coal tar pitch (CTP) and petroleum pitch-based CFs are high-strength, lightweight materials that are widely used in aerospace, automotive, and other industries. However, there are some important differences between these two pitches in terms of their use as carbon fiber precursors and in the production process. Table 1 shows some of the listed differences while their structural difference is shown on the next page, inferred from (Alcaniz-Monge et al., 1997; Frank et al., 2012; Kershaw & Black, 1993; Tadayuki Matsumoto & Mochida, 1992).

Table 1 Comparison between coal tar and petroleum pitches.

Difference	Coal Tar Pitch	Petroleum Pitch
Composition	Complex mixture of polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds. ^{1,2} Properties affected: strength, stiffness, and thermal conductivity.	Contains mainly aromatic hydrocarbons and some heterocyclic compounds. ^{1,2}
Softening point	Higher softening point- requires higher temperatures to melt and process. ^{2,3} Effect: production process more difficult and energy intensive.	Lower softening point- requires lower temperatures to melt and process. ^{1,3}
Yield	Has a higher carbon yield hence can produce more carbon fibers per unit of pitch. ^{1,2} Effect: quality of the resulting carbon fibers can be affected by the impurities and heterogeneity	Has a lower carbon yield thus can produce fewer carbon fibers per unit of pitch. ^{1,2,3}
Environmental impact	Contains high levels of polycyclic aromatic hydrocarbons (PAHs), which are considered carcinogenic and toxic to the environment. ^{1,3}	Contains fewer toxic compounds and has a lower environmental impact. ^{2,3}

¹(Kershaw & Black, 1993), ²(Tadayuki Matsumoto & Mochida, 1992), ³(Frank et al., 2012)

Coal Tar Pitch



Petroleum Pitch

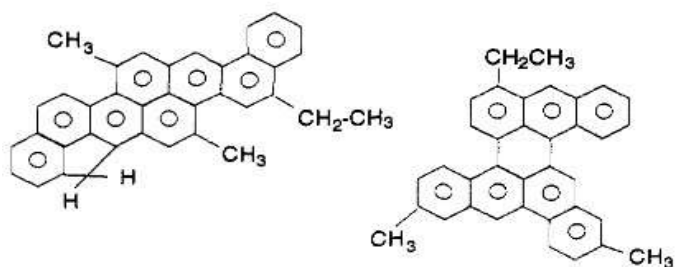


Figure 4 CTP and PP chemical structures

Reprinted with permission from (Kershaw & Black, 1993)

2.2.2. Brief Review of Petroleum and Coal Tar-Based CF

Below Tables 2 and 3 give an overview of the previous studies conducted and the features of the CF produced.

Table 2 Previous studies on petroleum and mesophase pitch-based CF production

Raw materials	Process/conditions	Products	Features	Reference
FCC slurry oil-heavy aromatic hydrocarbon (by-product)	Thermal condensation with in-process hydrogenation	-Mesophase precursor -Carbon Fiber	- Softening point rises from 87–118 to 239–297 °C - Concentrated extracted component distribution - Low softening point - Large domain and uniform structure - Optical structure improved - Ordered crystal structure	(Li et al., 2018)
Pitch & LLDPE	Melt spinning operated at 315 °C in single screw extruder	Carbon Fiber	- Softening point improvements not reported; melting point of the blend reduced from the main base material of 120 to 90–110 °C - Cheaper than PAN based - Reduced brittleness - Excellent thermal stability to 800 °C - Ductility increased by 25% -Improved tensile strength	(Aldosari et al., 2021)
Petroleum Pitch	MD simulations with ReaxFF using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)	Carbon Fiber	-Increased sp ³ fraction -High-density Carbon Fiber - Isometric compressive and tensile moduli CFs (~400 GPa) are best for compressive loading applications - Spinning temperatures set to 40 to 50 °C above pitch softening point	(Jana et al., 2022)
Naphthenic base vacuum gas oil	- High-pressure thermal treatment - Thermal condensation reaction	Mesophase precursor	-R1 had 87 % and the softening point was 289 °C with more alkyl side chains -R2 had 95 % and the softening point was 243 °C with more naphthenic groups *R1 and R2 are rich-aromatic distillates	(Li et al., 2015)

Asphaltenes	-Stabilization by means of oxidizing acids (HNO ₃ and H ₂ SO ₄)	- Overall yield of carbon fibers is 37 – 38 wt.% - Tensile strength and elastic modulus of 811 MPa and 32.7 GPa	(Leistenschneider et al., 2021)
Asphaltenes	-Autoxidation 190–250 °C -Bromination (150–170 °C) followed by debromination	- Slight change in Young's modulus - Increase in the melt spin productivity - Penetration depth decreased from 15.3 ± 0.4 mm to 3.4 ± 1.1 for asphaltenes	(Kim et al., 2021)

Table 3 Previous studies on CTP-based CF production

Raw materials	Process/conditions	Products	Features	Reference
Heavy oil residue	Bromination N ₂ –Blowing	-Pitch precursor -Carbon Fiber	-Softening point rises from 40 °C to 265 °C -Yield 43% -Enhanced aromaticity -Enlarged molecular size -Reduction in molecular mobility and optical isotropy	(Y. O. Choi & Yang, 2001b)
Anthracene oil	-Oxidative thermal condensation followed by thermal treatment -Melt spinning (spinning temperatures ranged within 260-285 °C)	Carbon Fiber	-Softening point of 247 °C -Pitch is totally ash free -High aromaticity index -Low Sulfur content -Low toxicity -Diameters smaller	(Díez et al., 2012a)
Coal tar pitch (CTP) and pyrolysis fuel oil (PFO)	- Modification by thermal treatment - Melt spinning process - Post spinning stabilization and pyrolysis process - Acid treatment before heating - Cross linking of the aromatic hydrocarbons by 30% O ₂ -Using boron trifluoride/triethyl etherate (BFDE) as catalyst and nitrobenzene as co-catalyst -Tar air blowing and thermal treatment	Pitch precursor	-Increased softening point -Increased yield of 70% and softening point of 290 °C with acid treatment -Increased yield of 32% and softening point of 280 °C with crosslinking -Anisotropy formation suppressed -214 °C as softening point and 0.77 aromaticity	(Banerjee et al., 2021)

Tetrahydrofuran (THF)/ Coal tar	- bromination–dehydrobromination -does not require complicated pre-treatments such as pressurization and vacuum distillation	-Isotropic pitch precursors	- More light components than CTP - Better polycondensation - Greater carbon aromaticity - Excellent spinnability - Softening point of 230 °C -Yield reduced by approx. 20% compared from 100% raw CTP	(J. Liu et al., 2022)
Coal tar	-Blowing air	-Isotropic pitch precursors	- 453-473 K with a good spinnability.	(Alcaniz-Monge et al., 1997)
Coal tar	-Blowing air in autoclave and heating at 330 °C, 360 °C and 380 °C	-Isotropic pitches	- Pitches blown at 360 °C for 2 to 4 h showed excellent Spinnability	(Maeda et al., 1993)
	-Further heating at 380 °C with N ₂	-Mesophase pitch -Anisotropic texture achieved	- Longer than 4 h at 330 °C to get a softening point of 280 °C, yielding 65%, and 2 h at 360 °C yielding 62% - Increase of aromatic hydrogens for 2–4h air blow from 86.5% to 89.7 and 91.9%, respectively and decrease of aliphatic hydrogens	
Hyper-coal	-After carbonization at 600 °C	-Isotropic pitch -Pitch based CF	-Satisfactory mechanical properties -Averaged tensile strength of 1150 MPa after heating to 800 °C for 5 min -Decreased their spinnability - Softening point of 210 °C and 250 °C	(Yang et al. 2016)
	-With 1-methylnaphthalene subjected to thin layer evaporation under the vacuum of 500 Pa at different temperatures below 300 °C for varying durations			

2.2.3. Cost of Raw Materials for CF Production

The pervasive profitable use of CFs is constrained by their soaring expense, which predominantly varies with the kind of carbon feedstock. Typical procedures for manufacturing CFs utilize costly raw materials, for instance hydrocarbons along with graphite. A feasible explanation to this difficulty is the use of coal, coal tar and petroleum as a useful precursor to yield CFs (Daulbayev et al., 2021). Precursor budget consumes over 50% of whole cost for CFs manufacture, embracing low-priced precursors for CFs have been exploited as one of the major approaches developing cheap CFs (Choi et al., 2019).

Even with effective use of Carbon Nano-Materials (CNMs), the progress of economical and ecologically welcoming techniques for their groundwork is a substantial challenge. Contemporary machineries for creating Carbon Nano-Materials regularly demand the usage of pricy resources, which precisely influence their cost. Consequently, the improvement or advancement of procedures for creating Carbon Nano-Materials by making use of inexpensive materials is of remarkable relevance in the perspective of engineering focus and is a precedence undertaking of several scientific parties (Daulbayev et al., 2021).

According to Daulbayev et. al. 2021, the processes for making CFs as per mesophase and isotropic pitches necessitate radical latest methods towards enhancing their physiochemical characteristics. For instance, the purpose of mesophase pitch will result in considerable rise in value owing to the exceedingly complicated procedure of its fabrication and low production, around 10% by weight. Though recent ways of acquiring

mesophase pitch, for example supercritical removal in the company of toluene and getting AR-mesophase pitch, could substantially improve the return, almost 20% by weight, the expense persists on the elevated degree. Different from carbon fibers built on mesophase pitch, fibers made of isotropic pitch possess inadequate mechanical features.

A conceivable resolution to the challenges illustrated earlier is conceptualizing intricate composite forms based on C-CFs, which will not just certainly affect the qualities of fibers, but also notably lower their cost. Currently, agreeing to information from public resources of exchange programs, it can be observed that the amount of pitch fluctuates between \$ 250 and \$ 755 for a thousand kilograms of manufactured goods. Charges vary based on the concentration of the product, along with on the kind of source as well as the molecular positioning of the pitch, either isotropic or mesophase. It ought to be stated that the cost for 1,000 kg of mesophase pitch can be not less than 3 folds than the price of isotropic pitch (Daulbayev et al., 2021).

The benefit of coal tar pitch-based CF is that the raw material is economical as compared to PAN. On the other hand, PAN based fiber is costly, thus, increases the price of the final commodities. But coal tar pitch-based CF can be an appropriate choice for the reason that it has cheap raw material (Banerjee et al., 2021).

2.2.4. Pre-treatment Methods

Pre-treatment is an important step in CF production as it prepares the precursor material for the subsequent heating and oxidative stabilization steps. Pre-treatment methods typically involve chemical and/or physical processes that modify the precursor material to

improve its thermal stability and promote the formation of carbon-rich structures. Various pre-treatment methods have been used and reported to obtain precursors. Some of the companies like Toray and Nippon Graphite Fiber Corp. from Japan, BASF from US among others have been successful in producing desired CFs and raw materials. In terms of conversion chemistry, thermal pre-treatment is used to increase the carbon content through hydrogen disproportionation and the release of volatile more hydrogen-rich products (Frank et al., 2012; Kim et al., 2021; Mirdehghan, 2021).

According to reports, coal tar pitch contains an abundance of aromatic molecules attached to very few aliphatic side chains, whereas petroleum pitch contains polycyclic aromatic hydrocarbons with more aliphatic chains as shown in Figure 4 (Kershaw & Black, 1993; D. Liu et al., 2018; Zhang et al., 2015) .

The pre-treatments take place during oxidative stabilization, also known as the stabilization step, in which the green fibers are oxidized in air at temperatures ranging from 30-50 °C below the softening point of the precursor to 300 °C. This step initiates oxidative cross-linking reactions between heteroatom-containing groups, which stabilize the fiber structure (Li et al., 2015; Senda et al., 2019; Tadayuki Matsumoto & Mochida, 1992; Yuan et al., 2017). In the production sequence leading to carbon fibers, the pre-treatment step comes before melt spinning. Generally, there are several typical pre-treatment methods used in CF production, examples are as shown in Figure 6 (Bermudez et al., 2018; Bhatt & Goe, 2017; Park, 2015):

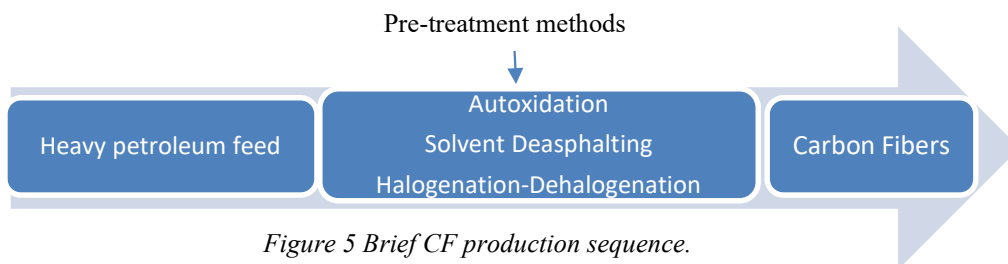


Figure 6 Typical pre-treatment methods used in CF production.

A pre-treatment step has the advantage of allowing the material to be converted into a fluid instead of a solid. The discharge of volatile products has little or no effect on the shape or integrity of the fiber because it is produced only after the pre-treatment step. A pre-treatment step may also shorten the duration of the stabilization step after melt spinning, reducing the total cost of the process (Kim et al., 2021).

A suitable stabilization process must be found based on the starting material, its composition, and its softening point. Because the oxidative process step takes the most time and money, efforts have been made to shorten it (Khayyam et al., 2020). Yonemoto et al. discovered, for example, that adding NO_2 to the air atmosphere increases the oxidation degree of the fibers. Based on these findings, it was demonstrated that treating petroleum pitch-based green fibers with dilute HNO_3 can significantly reduce oxidation time from 60 to 6 h (Leistenschneider et al., 2021). Under moderate conditions, autoxidation and halogenation could be performed at 250 °C, and scale-up is possible using bubble column reactors. The need for hydrogen halide recovery and recycling, including the use of far more specialized building materials, have been well-known detractors in the scenario of halogenation (Kim et al., 2021; Suresh et al., 2000).

Regrettably, halogenation was less likely than autoxidation to remove carbon. In contrast to halogenation, autoxidation may help decrease carbon fiber production by lowering carbon content via carbon monoxide and carbon dioxide elimination (Kim et al., 2021).

2.2.5. Challenges of Petroleum-Pitch-Based Carbon Fiber

The rheological properties of heavy oils as well as the physical characteristics of their reservoirs make its manufacture a task in the oil industry (Santos & Lo, 2014). Production projects have to face technological trials in all phases of operation: reservoir, transportation and refining (Saniere et al., 2004).

The complexities of heavy petroleum arise from the fact that it requires more complex refining processes than lighter crude oils to produce usable fuels and other products. The following are some of the main challenges associated with heavy petroleum (Encyclopedia Britannica, 2022; Houda et al., 2018; James G. Speight, 2014; Rodgers & McKenna, 2011):

- i. Variable composition- usually varies widely depending on the source and the specific extraction process used. This can make it difficult to predict the quality and properties of the resulting products.
- ii. High acidity- some can be highly acidic, which can cause corrosion and damage to equipment used in refining and processing. Specialized materials and processes are required to mitigate these effects.
- iii. High viscosity- its high viscosity makes it difficult to extract, transport, and process. It requires specialized equipment and processes to overcome these challenges.
- iv. High sulfur content- it often contains high levels of sulfur compounds, which can have negative environmental impacts and contribute to air pollution. Specialized refining processes, like hydrotreating, are required to remove sulfur from heavy petroleum.

- v. Environmental impact- examples are oil spills and air pollution. Efforts are underway to reduce these impacts through improved extraction, transportation, and refining practices.

Despite these complexities, heavy oils remain an important source of energy and raw materials for a range of industries and applications, one being CF production. Efforts are underway to develop more efficient and sustainable processes for extracting and refining heavy petroleum, as well as to explore alternative sources of energy and materials (Kim, 2021; Kim et al., 2021).

2.3 Autoxidation Chemistry

Autoxidation of heavy petroleum refers to the spontaneous oxidation process that occurs in the presence of atmospheric oxygen and leads to the formation of products following free radical pathway (Montoya Sánchez & de Klerk, 2018). The reaction may be either catalytic or non-catalytic. In this study, the focus was on non-catalytic. Non-catalytic autoxidation proceeds through a complex network of free radical reactions that includes initiation, propagation, and termination steps (De Klerk, 2003; Ingold, 1967; Siddiquee et al., 2016).

2.3.1. Reaction Mechanism

The process of a chemical reaction can be broken down into three main steps: initiation, propagation, and termination. These steps describe how reactant molecules, in this case hydrocarbons, interact with each other and how products are formed. Below are

the steps with equations and explanations (Emanuel et al., 1969; Steven Farmer et al., 2023; Tobolsky et al., 1949).

2.3.1.1. Initiation

The initiation step involves the formation of highly reactive species from stable reactants. These species are typically formed through the input of energy, such as heat, light, or a catalyst. The reactive species can then go on to react with other molecules to form products. The equation for an initiation step typically involves the formation of a reactive intermediate. An example is the formation of free radicals that occurs as a result of the reaction between hydrocarbons and molecular oxygen. During this process, the molecular oxygen reacts with the hydrocarbons to remove hydrogen atoms, resulting in the formation of alkyl radical and hydroperoxyl radical species (De Klerk, 2003; Emanuel et al., 1969; Steven Farmer et al., 2023):



2.3.1.2. Propagation

The propagation step involves the reaction of the highly reactive intermediate with other reactant molecules, leading to the formation of new intermediates and products. The intermediates formed in the propagation step can go on to react further, leading to a chain reaction. The equation for a propagation step typically involves the reaction of the reactive intermediate with a stable reactant to form a new intermediate and a product. An example of such is the free radicals generated in Reaction (1) undergo a reaction with hydrocarbons and oxygen, leading to the creation of additional free radicals according to the following processes (De Klerk, 2003; Steven Farmer et al., 2023):

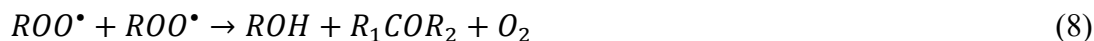


Whereby in chain propagation by alkyl hydroperoxides the most crucial reaction is the radical-induced decomposition as shown in Reaction (5) (De Klerk, 2003):



2.3.1.3. Termination

The termination step involves the removal of highly reactive intermediates or the combination of two intermediates to form stable products. The termination step is important for preventing the reaction from continuing indefinitely and consuming all of the reactants. The equations for a termination step typically involve the removal or combination of intermediates, as shown in Reactions 6–8 (Emanuel et al., 1969; Steven Farmer et al., 2023).



The specific product that results from the termination step is contingent upon the experimental conditions. Under such conditions, oxygenates exhibit greater reactivity than the feed hydrocarbons and yield secondary products, as illustrated in Figure 7.

2.3.2. Hydrocarbon Autoxidation

Figure 7 shows the reaction pathways for the autoxidation reaction. The oxygen availability in free radical oxidation chemistry is important in free radical formation via H-abstraction (initiation) and subsequent propagation steps. If oxygen is available after the free radical formation reaction, the reaction proceeds to step 3; otherwise, the reaction proceeds to the addition (heavier) product formation (step 2). Autoxidation can be used to control the product selectivity - heavy (addition) products or products with oxygen functional groups - based on this fundamental understanding. Autoxidation of heavy petroleum would follow the free radical mechanism; oxygen availability could show how it would work either step 2 or step 3 (Siddiquee et al., 2016).

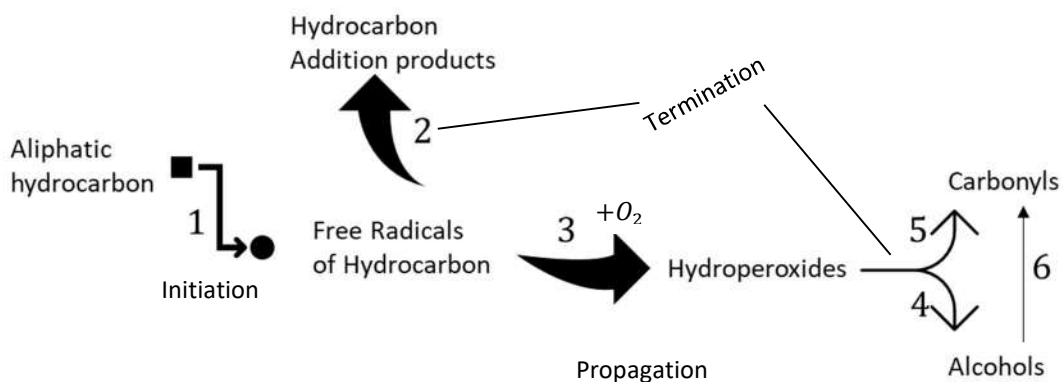


Figure 7 The aliphatic hydrocarbon autoxidation reaction network.
(Siddiquee et al., 2016)

In terms of refining, the hydrogen-to-carbon ratio is commonly used to determine petroleum grade. The H/C ratio also shows the degree of unsaturation, which decreases from conventional crudes (usually greater than 1.8) to unconventional crudes (usually 1.4 to 1.6 for heavy petroleum) (Strausz & Lown, 2003). The presence of aromatic structures

in heavy petroleum is also indicated by the lower H/C ratio. The presence of naphthenic-aromatic compounds and a lower number of paraffinic compounds in heavy petroleum is also indicated by hydrogen-to-carbon ratio of 1.5 (Kim et al., 2021; D. Liu et al., 2018; Strausz & Lown, 2003).

The C–H bond present at the position of the aromatic ring is weak and more susceptible to H-abstraction to produce comparatively stable free radicals, which is one of the key characteristics of the naphthenic-aromatic hydrocarbon (Siddiquee & de Klerk, 2014). Asphaltenes, like common H-donor solvent tetralin, exhibit the H-donating phenomenon due to the presence of naphthenic-aromatic compounds (Fong et al., 2020). Furthermore, previous research has shown that due to the presence of stable free radicals, this compound class may have formed an addition product via olefin formation following H-disproportionation as shown in Figures 8 and 9 (Siddiquee & de Klerk, 2014).

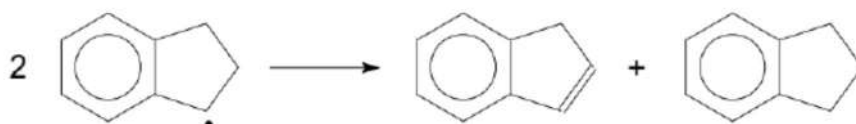


Figure 8 Naphthenic-aromatic compound-indan by hydrogen disproportionation.

(Siddiquee & de Klerk, 2014)

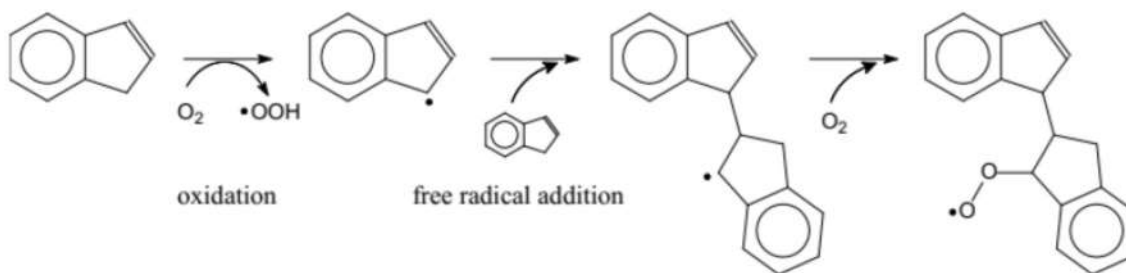


Figure 9 Reactions of naphthenic-aromatic compound-indene oxidation and free radical addition.

(Siddiquee & de Klerk, 2014)

With the removal of light fractions, the synergistic effect between pitch components in melting was significantly reduced, resulting in a decrease in pitch spinnability and deterioration of carbon fiber microstructure uniformity. With the removal of light fractions, the oxidative reactivity of pitch fibers gradually decreased. The reason for this was that light fractions had more alkyl side chains, which were preferentially attacked by oxygen at low oxidation temperatures, than heavy fractions (Alcaniz-Monge et al., 1997; Chai et al., 2022; Kim et al., 2021)

Heavy petroleum fraction autoxidation is not a novel technique. The majority of the reported studies were conducted to develop in situ heavy petroleum recovery (H.H. XU et al., 2001; Jia et al., 2016), to comprehend hardening in relation to road construction (Herrington, 1998; Petersen & Glaser, 2011; Tauste et al., 2018), as well as upgrading heavy petroleum through oxidative sulfur and nitrogen removal (Hu & Yu, 2015; Javadli & de Klerk, 2012). The autoxidation of heavy petroleum fraction resulted in a few chemical and physical changes, such as an increase in viscosity (Babu & Cormack, 1983; Javadli & de Klerk, 2012; Siddiquee & de Klerk, 2014), and increased asphaltene content (H.H. XU et al., 2001; Jha et al., 1978; Moschopedis & Speight, 1975).

The naphthenic-aromatic hydrocarbon class was thought to be responsible for bitumen hardening or viscosity increase (Siddiquee & de Klerk, 2014). Though some O-incorporation as a functional group could perhaps have an effect on viscosity, (Herrington, 1998; Petersen & Glaser, 2011). However, it was discovered that viscosity rise might also result during the model reaction (heating bitumen in the nitrogen's presence) (García Zapata & De Klerk, 2014). Prolonged autoxidation of oilsands bitumen at 130 °C for 229 hours with air led to an extreme viscosity increase that was roughly 12 times. Moreover,

bitumen later turned into a rock that was nearly 17 times harder than the source material (Siddiquee & de Klerk, 2014). Furthermore, heteroatoms containing a portion of the bitumen (for example, N, S, and O) exhibit addition product formation (Figure 10) (Siddiquee & De Klerk, 2015):

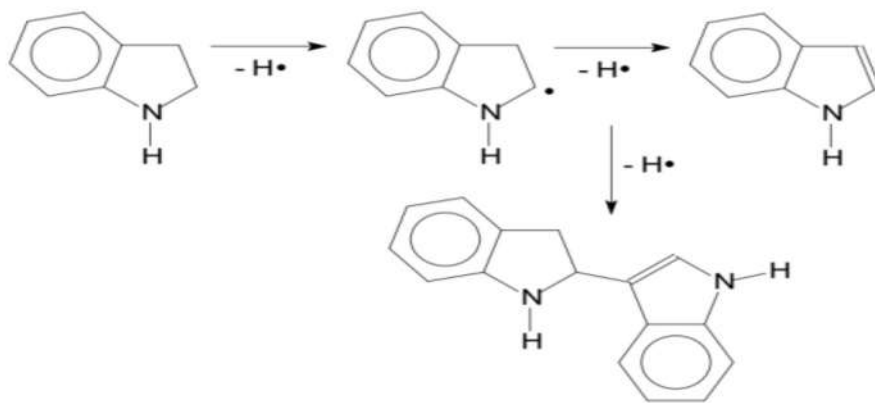


Figure 10 Dimerization of 2,3-dihydroindole during autoxidation due to H abstraction

(Siddiquee & De Klerk, 2015)

The viscosity of Athabasca bitumen increased during oxidation with air, oxygen, and ozone (Hendessi & de Klerk, 2016). Whilst increased viscosity and bitumen toughening are disadvantageous in terms of upgrading, there is ample opportunity to begin planning petroleum-based precursors for carbon fiber production by boosting molecular weight distribution and aromaticity (Siddiquee & de Klerk, 2014) and crosslinking, resulting in a higher softening point of heavy petroleum fractions. -The dehydrogenative polymerization is also supported by a study of chemical changes in coal tar pitch during mild air oxidation (Barr & Lewis, 1978).

Every one of the pieces of evidence suggests that restricting the oxygen supply just after initial free radical formation can improve the heavier product selectivity. In many

instances, the amount of oxygen available can be influenced to promote the formation of additional (heavier) products (Shah et al., 2015). The heavier product obtained could have had a higher molecular weight, aromaticity, and cross linking, leading to an increased softening point, making it useful as a CF precursor from heavy oil fractions. No additional chemicals are required for the suggested model. Because the air was the only oxidant it would have been more cost-effective and environmentally friendly than the established chemical-based carbon fiber precursors derived from pitch (Y. O. Choi & Yang, 2001a; Liang et al., 2020).

2.3.3. Factors Affecting Autoxidation

Hydrocarbon autoxidation is influenced by a range of factors that can affect the reaction rate, product distribution and selectivity, and reaction mechanism. Some of the primary factors include (Asinger, 1968; Helberg & Pratt, 2021; Siddiquee et al., 2022):

- i. **Oxygen Concentration:** Higher oxygen concentrations can lead to more rapid and extensive autoxidation of hydrocarbon forming alcohols and ketones as in Figure 7. Product selectivity is highly controlled by the amount of oxygen present in the system.
- ii. **Temperature:** With higher temperatures generally leading to more rapid autoxidation, the specific effect of temperature can vary depending on the hydrocarbon structure. However, the temperature is significant in regulating how fast the reaction would take place.

- iii. **Presence of Catalysts:** Certain catalysts, such as transition metal ions, can promote autoxidation by facilitating the formation of free radicals.
- iv. **Reaction time (space-time):** The rate of autoxidation of hydrocarbons is influenced by the reaction or space time, as a longer reaction time or larger reaction vessel volume can provide more opportunities for the hydrocarbons to react with oxygen, leading to increased oxidation rates. Besides, reaction time may be reduced if the temperature is elevated.
- v. **Pressure:** Increasing pressure can increase the rate of autoxidation reactions. This is because higher pressure increases the concentration of reactants, leading to more frequent collisions and higher reaction rates. Additionally, increasing pressure can also affect the thermodynamics of the reaction, favoring the formation of products with higher boiling points.

However, the effect of pressure on hydrocarbon autoxidation can be complex and can depend on a variety of factors, such as the specific hydrocarbon being oxidized, the presence of other chemical species (such as catalysts or inhibitors), and the temperature and pressure conditions being used. As such, the impact of pressure on hydrocarbon autoxidation must be evaluated on a case-by-case basis and may require experimental testing to determine its exact effects (Asinger, 1968).

A typical phenomenon was demonstrated in a recent oxidation study of naphthenic-aromatic hydrocarbon-tetralin in a microfluidic reactor (de Klerk, 2011; Siddiquee et al., 2022). It was possible to manipulate the oxygen availability to increase the ketone-to-alcohol ratio to 14:1 instead of 1:1. At higher oxygen availability, it was possible to control the addition product selectivity (Siddiquee et al., 2016). While controlling the addition

product selectivity, Indan, another naphthenic aromatic hydrocarbon with a five-member ring compound class, demonstrated similar product selectivity even at higher conversion. This microfluidic reactor study also highlighted the importance of oxygen availability and mixing in conversion and product selectivity. Lack of mixing is a major factor in the formation of addition products (Siddiquee et al., 2020).

2.4 Research Gap

One of the major research gaps in the field of HVGO oxidation is the lack of understanding of the effect of thermal and time parameters on the controlled autoxidation reaction. Current literature has focused on the PAN and CTP-based CF, but there is a dearth of studies that investigate impact of temperature, reaction time, partial pressure of oxygen (P_{O_2}) and gas-liquid (G-L) interfacial area. This knowledge gap is critical since it limits the optimization of reaction conditions to enhance yield and selectivity of desired products.

Whereby importance of this research has aimed to investigate the effect of thermal and time parameters on HVGO oxidation and P_{O_2} through G-L interfacial area. By filling this research gap, the study has provided a comprehensive understanding of the HVGO oxidation process, leading to the development of optimized reaction conditions. This, in turn, has enabled the production of high yields of desired products and reduced the formation of unwanted byproducts. Also, the findings of this research can be applied in the petroleum industry to improve the efficiency of HVGO oxidation, which is crucial for meeting the increasing global demand for energy and lessening the costly production of CF.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The feed material used in this study, which included HVGO, VGO, and HT-VGO, was obtained from Saudi Aramco. The raw materials were stored in dark in order to minimize exposure to light since it reduced the impact of free radical reactions induced by light, which could result in an increase in oxidized heavy oils formation through processes such as photooxidation (Glattke et al., 2020). The following illustrates the procedure used to perform the autoxidation experiment. The feed material was examined before utilization. Table 4 displays the traits of the raw material used in the study. The standard deviation figures indicated represent the repeatability of the assessments, which were conducted three times.

Table 4 Properties and Composition of Material Feed^a

Property	Raw HVGO wt.%
Carbon	85.3
Hydrogen	11.9
Nitrogen	0.1
Oxygen ^b	0.4
Sulfur	2.3

^a Tests were repeated three times, and the results were recorded as the average $\pm$ one standard deviation of a single sample. ^b Content of was obtained by the difference.

The cylinder gases used for the autoxidation reactions were ultrahigh purity nitrogen (99.999% purity, batch no. N08/02/2022-29) supplied by Air Liquide Al Khafrah Ind. Gases and compressed zero air by Saudi Industrial Gas Company. Besides, the following chemicals were also used for cleaning glassware after the experiments: $\geq 99.8\%$ chloroform from Honeywell, $\geq 99.8\%$ acetone from Sigma-Aldrich of Cat. 34850-1L, $\geq 99.7\%$ toluene of Cat. 32249-1L, 36% hydrochloric acid, 98% sulfuric acid, and 86% nitric acid from Honeywell. Whereas 99.7% benzene and 99.9% carbon disulfide from Honeywell were utilized in dissolving the samples for analyses.

3.2 Equipment and Procedure

The apparatus consists of a 250 mL three-neck round-bottom flask made of Pyrex. The first neck of the flask was attached to an air (or N₂) supply line, the second neck was connected to a condenser with the cooling fluid set to 8 °C, and a thermocouple was inserted through the third neck to measure and control the sample temperature directly during the oxidation process. A Heidolph MR Hei-Standard heat-on-block heater with a magnetic stirring system was used to control the temperature and mixing in the flask. A magnetic stirring bar was used for mixing at 250 rpm. The air was sourced from a compressed air cylinder and the airflow rate was adjusted to 140 mL/min by a flow meter (PMR 1-010977, Alaborg Instrument, USA) with and without bubbling into the petroleum fractions. Without bubbling (called in this manuscript as blowing) was used to investigate the effect of mixing and gas-liquid interfacial per unit liquid volume.

About 50 g of the raw material was loaded into the three-neck round-bottom flask. The flask with the heavy petroleum fraction was heated to the reaction temperature by Heidolph MR Hei-Standard heat-on-block. A very small amount of silicone oil was used to improve the contact between the glass and metal surfaces. The selected reaction temperatures ranged from 130 to 260 °C. The raw material was preheated to the reaction temperature, the air supply line was opened, and the reaction time was started. The raw material was magnetically stirred at the stirring speed of 250 rpm by the Heidolph MR Hei-Standard Hot Plate Stirrer during the reaction at 200 °C and 260 °C, in which the raw material had low enough viscosity to be stirred. Reaction times were between 4 to 48 h. At the end of the reaction time, the air supply line was shut off, and the product was left in the fume hood to cool.

To check if the heating itself had an effect, control experiments using an inert nitrogen atmosphere were carried out for the different reaction times ranging from 4 to 48 h. The control experiments were carried out in the same way as the autoxidation reactions except there was no air supply line, and prior to heating, the flask with the raw material was flushed with nitrogen.

To achieve the objectives of the study, selected parameters were examined analytically, and their outcome were elaborated herein. The experimental setup in Figure 11 was used in generating the oxidized products of the heavy petroleum feeds: VGO, HT-VGO and HVGO. Some improvements were implemented to enhance process performance and ensure quality products. Any random or systematic errors observed were however, minimized to ensure quality products by employing several cautious steps.

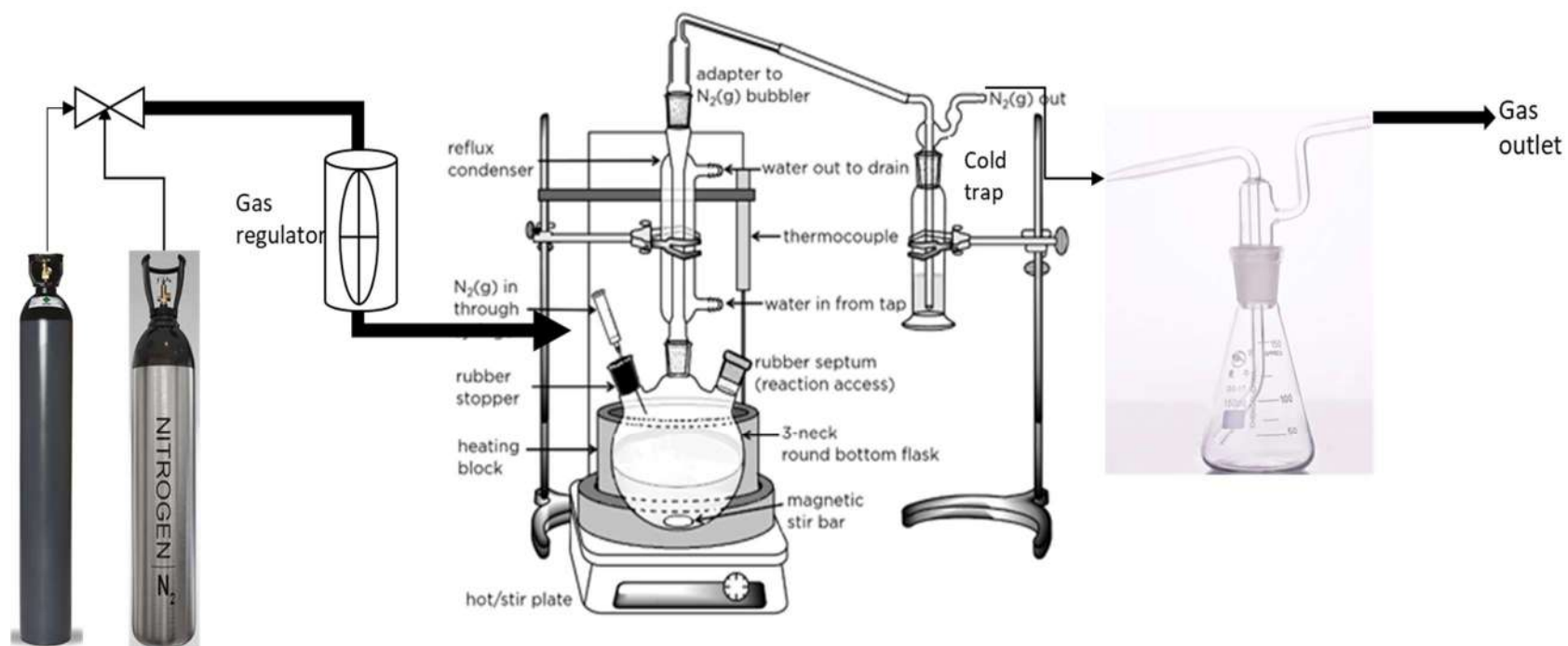


Figure 11 Experimental schematic setup.

3.3 Sample Experiments

Table 5 summarizes the number of experiments that were run to fabricate the precursors.

Table 5 Experiment details and operating conditions

Experiment No.	Time, h	Temperature, °C	Gas	Flow	Feed
1	6	130	N ₂	Bubbling	VGO
2	6	130	Air	Bubbling	VGO
3	6	130	N ₂	Bubbling	HT-VGO
4	6	130	Air	Bubbling	HT-VGO
5	48	130	N ₂	Bubbling	HVGO
6	48	130	Air	Bubbling	HVGO
7	24	130	N ₂	Bubbling	HVGO
8	24	130	N ₂	Bubbling	HT-VGO
9	24	130	Air	Bubbling	HVGO
10	24	130	Air	Bubbling	HT-VGO
11	24	130	Air	Bubbling	VGO
12*	4	200	Air	Bubbling	HVGO
13	4	220	Air	Bubbling	HVGO
14	4	240	Air	Bubbling	HVGO
15*	4	240	N ₂	Bubbling	HVGO
16	4	250	Air	Bubbling	HVGO
17	4	240	Air	Bubbling	HVGO
18*	8	200	Air	Bubbling	HVGO
19	8	220	Air	Bubbling	HVGO
20	8	240	Air	Bubbling	HVGO
21*	8	260	Air	Bubbling	HVGO
22	4	200	N ₂	Blowing	HVGO
23	4	200	Air	Blowing	HVGO
24	4	240	N ₂	Blowing	HVGO
25*	4	240	Air	Blowing	HVGO
26	4	260	N ₂	Blowing	HVGO
27	4	260	Air	Blowing	HVGO
28	8	200	Air	Blowing	HVGO
29	8	260	Air	Blowing	HVGO
30	8	240	Air	Blowing	HVGO
31	24	200	Air	Blowing	HVGO
32*	24	240	Air	Bubbling	HVGO
33	4	220	N ₂	Bubbling	HVGO
34	4	200	N ₂	Bubbling	HVGO
35	8	200	N ₂	Bubbling	HVGO
36	8	240	N ₂	Bubbling	HVGO

*Repeated/reproduced for reproducibility studies

3.4 Sample Calculations

One of the calculations was the manual measurement of the density of raw HVGO by immersing it in water (at room temperature) calculated as (G. R. Blake, 1965):

$$\text{Density}, \rho = \frac{\text{Mass}, m}{\text{Volume}, V} \quad (9)$$

The weights before wrapping and after parafilm with HVGO were measured by digital weighing scale and their masses in grams were recorded. A parafilm of measurements $50 \times 50 \times 0.12$ mm was utilized to wrap an unknown amount of raw HVGO and fully immersed in a 25 mL glass measuring cylinder filled with water to the 10 mL mark. About 8 mL of water was displaced and below is the determination of the bulk density of raw HVGO:

Table 6 Bulk density calculation values for raw HVGO

Parameter	Weight, g	Parameter	Volume, cm ³
Mass of empty parafilm	0.3062	Water displaced	0.8
Mass of filled parafilm with raw HVGO	0.8675	Volume of parafilm	0.3
Mass of raw HVGO	0.5613	Volume of raw HVGO	0.5

Thus, bulk density found was ~ 1.12 g/cm³ which is in the range of those reported in literature too (G. R. Blake, 1965; Kim, 2021).

3.5 Characterization and Analysis

Product characterization is the process of determining the physical and chemical properties of a product. The goal of product characterization is to understand the composition, structure, and behavior of a product in order to optimize its quality,

performance, and safety. There are several techniques and tools used for product characterization, including spectroscopy, chromatography, thermal analysis, and mechanical testing. These techniques can be used to measure properties such as composition, chemical structure, molecular weight, aliphaticity and aromaticity, melting point, thermal stability, and softening point. The techniques used to analyze samples and products in the current study are as follows:

3.5.1 Viscosity

In this study, a Discovery HR-3 hybrid rheometer (TA, USA) software with 40 mm Peltier parallel plate made of steel was utilized. The viscosity values were inserted to measure viscosities of the samples at 40 °C. Flow peak hold- a temperature of 25 °C with zero seconds soak time for 3 minutes and 10.0/s shear rate as test parameters, this measuring step to last for 10 minutes. Flow temperature ramp- starting at 25 °C at 5 °C/min ramp rate ending at 40 °C at 10.0/s shear rate and sampling interval of 10.0 s/pt with 4 minutes soak time after ramp to be completed in 7 minutes. Flow peak hold- measuring at 40 °C for 10 minutes with 3 minutes soaking time, at 10.0/s shear rate and sampling interval of 10.0 s/pt. End of test, the instrument cooled to 25 °C. Results of the samples as illustrated and elaborated in Sections 4.1.1, 4.2.1, 4.3.1 and in Appendix-A.

3.5.2 Aromaticity

The aromaticity of oxidized HVGO can be determined or measured using several analytical techniques, however in this examination the following were used:

- i. Less than 1 g was dissolved in deuterated chloroform and analyzed both in Proton and Carbon Nuclear Magnetic Resonance (^1H and ^{13}C NMR) Spectroscopy where the determination of the relative ratio of aliphatic (non-aromatic) to aromatic compounds in selected samples of raw and oxidized HVGO were conducted. Both ^1H and ^{13}C -NMR's were performed by dissolving about 0.5 g of material into 0.5 mL of deuterated chloroform (99.8%, Honeywell). A 5 mm ID, 7-inch-long borosilicate glass sample jet NMR tubes (Norell) with cap was used to perform the analysis in Bruker NMR 400 MHz - AVANCE 3.
- ii. Also, about 1 ml of each sample was dissolved in pure CS_2 in a 5ml vial. A drop from each of the samples tested independently in a Nicolet iS50 FT-IR analyzer by analyzing the absorption of infrared radiation at specific wavelengths and results as shown in Sections 4.1.3 and 4.2.3.

3.5.3 Boiling Point Ranges

In this study, about 1 g of each of the products, separately, was completely dissolved in (~4.5 mL) Carbon Disulfide (CS_2) and filled in 5 mL vials. The samples were tested using an Agilent ASTM D2887 SimDis-2 with Compass CDS w/ Eclipse SIMDIST

software and carrier gas of Helium at 20 ml/min and injection volume of 0.5 μ l. With ramp temperature of 20 $^{\circ}$ C/min to 600 $^{\circ}$ C, with column of DB-1, 10 m $\times$ 530 μ m $\times$ 2.65 μ m. This analysis resulted in highlighting the crucial boiling point ranges for the different oxidized products. The results are described in Sections 4.1.2, 4.2.2 and 4.3.2.

3.5.4 Thermogravimetric Analysis

Besides, to understand the extent of cross-linking which led to high molecular weight heavy product addition compounds, the thermal stability of such samples was insightful and provided guidance. About 10–20 g of selected samples was examined in a SDT Q600 V20.9 Build 20 whereby Differential Scanning Calorimetry (DSC) coupled with Thermogravimetry Analysis, using Alumina pan, injecting nitrogen at 50.0 ml/min, in a temperature range of 0–950 $^{\circ}$ C with ramp setting at 10.0 $^{\circ}$ C/min. TGA-DSC thermograms were produced and results elaborated in Section 4.1.4, 4.2.4 and 4.3.3.

3.5.5 Softening Point

To measure softening point of both HVGO and product samples, about 15–20 g of pre-heated material was filled in metallic ring and allowed to cool down in a refrigerator about -5° C for at least 30 minutes. Any additional protruding material after freezing was scrubbed off by a sharp flat thin plate. By using both manual ball-and-ring in a medium of glycerin, and Softmatic Automatic Ring & Ball by Mod. No. B070N2 (50/60 Hz, 800W) by MATEST S.p.A, Treviolo, 24048 Italy, softening points were recorded, and results analyzed herein in Sections 4.1.5, 4.2.5 and 4.3.4.

CHAPTER 4

RESULTS AND DISCUSSION

The chapter delves deeper into the scientific rationale by interpreting the obtained results. Each objective has been presented separately and later on merged to check the verification and/or validation of the formulated hypothesis.

4.1 Effect of Temperature and Time

Firstly, the objectives of the study were to be achieved by examining various properties and one of these properties is viscosity of product samples, their volatility, aromaticity, softening point and cross-linking.

4.1.1 Changes in Viscosity

The three different feed materials used here had their viscosity measured at 40 °C as shown in Figure 12. HVGO, the main feed of the study was the most viscous with measured viscosity of 729.6 cP due to its denser chemical composition than VGO and HT-VGO.

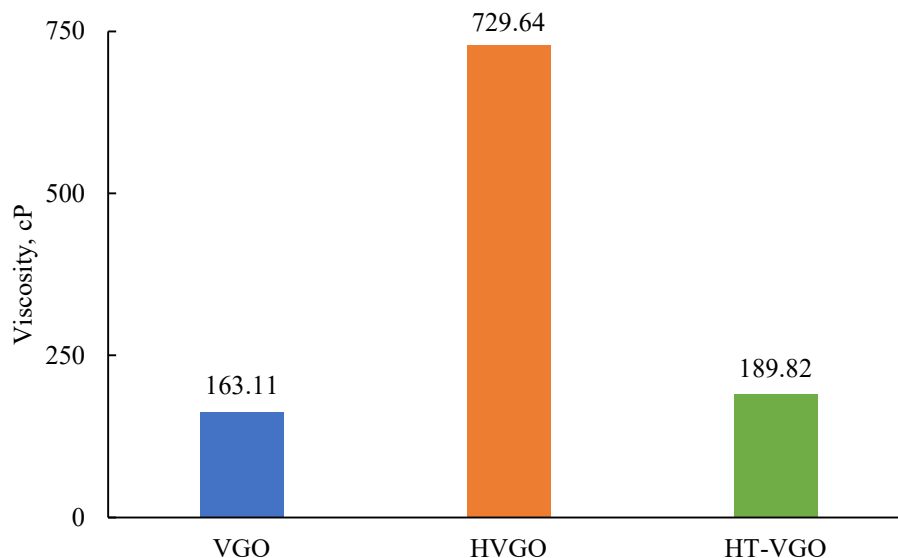


Figure 12 Viscosity of feed materials used in the study.

The resistance to flow is one property that was convicted to change during the process as addition products possess difficulty to move due to thickening, such is illustrated herein. In (Figure 13), HVGO samples autoxidized by air showed increase in viscosity when heated between 130–200 °C for 4 to 48 hours, the highest at 130 °C and 48 hours with measured viscosity of 1979.9 cP. However, those heated in the presence of N_2 exhibited a less considerable increment trend, an increment of measured viscosity from 995.1 to 1019.2 cP and 763.2 to 782.8 cP. This slight increment is clearly observed from the 4–8 hours at 200 °C and 24–48 hours at 130 °C samples respectively but a considerable increase when autoxidized by air. In (Figures 13–14), most of the samples oxidized by air showed a substantial upward trend with increase in temperature and time, with the highest recorded measured viscosity of 1979.9 cP, at about 130 °C for 48 h.

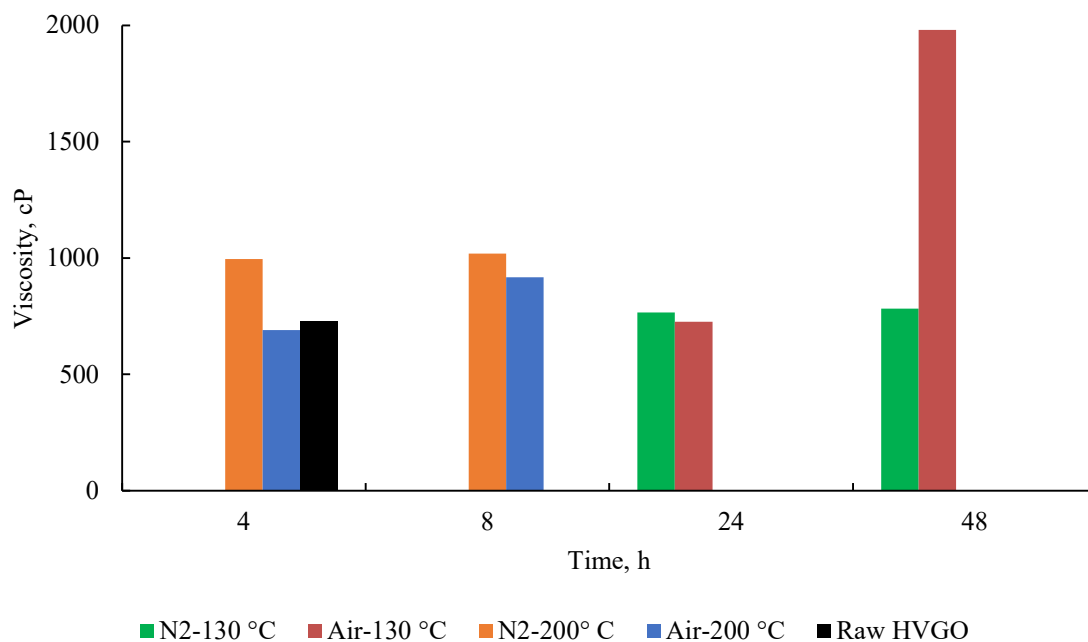


Figure 13 Viscosity changes measured at 40 °C of oxidized samples by air and N2 from 4–48 h, between 130 °C and 200 °C.

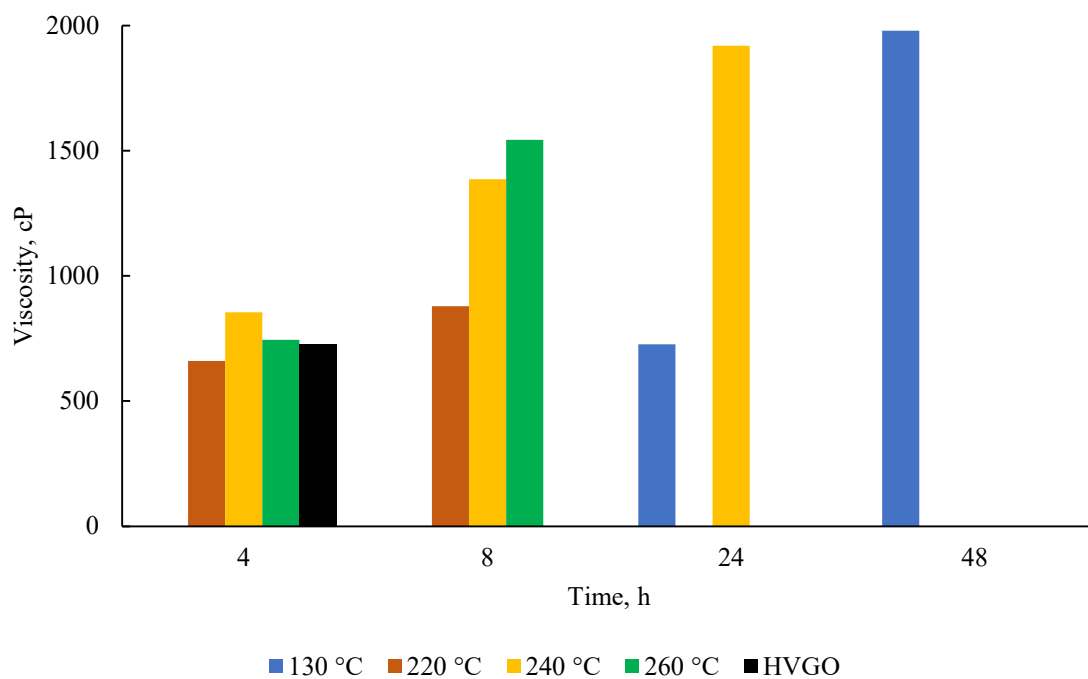


Figure 14 Viscosity changes of raw HVGO and oxidized samples by bubbling and mixing air from 4–48 h and between 130 °C and 260 °C.

Oxidation of HVGO can occur due to exposure to air, heat, or other environmental factors, which can change its properties and behavior. The effect of oxidation on the viscosity of HVGO depends on the extent and nature of the oxidation reaction (Lam-Maldonado et al., 2023). In a few cases, oxidation can break down the large, complex hydrocarbon molecules into smaller, less viscous ones, which can lead to a decrease in viscosity just as those heated at low temperatures and/or small durations (*in this case 130 °C in 24 h and 220 °C in 4 h*) (Khansari et al., 2012). This is often the case when the oxidation is mild and selective, targeting specific hydrocarbon groups (Lam-Maldonado et al., 2023; Shahbazi et al., 2006). Besides, it is also believed that the dissolution of and CO_2 could lead to a decrease in the viscosity of the resulting products (Lam-Maldonado et al., 2023; Strelets & Ilyin, 2021a)

However, in other cases, oxidation can result in the formation of heavier compounds that are more viscous than the original HVGO molecules, these heavier molecules could sometimes aggregate and solidify as reported in some studies, leading to an increase in viscosity (Kraiwattanawong et al., 2009; Strelets & Ilyin, 2021a). This can happen when the oxidation is more extensive and leads to the formation of heavy, complex compounds. The increase in viscosity of oxidized HVGO at higher temperatures would be due to the formation of complex, high molecular weight compounds such as asphaltenes. Asphaltenes are the heaviest and most complex molecular components of crude oil and are naturally present in HVGO (James G. Speight, 2014; Rodgers & McKenna, 2011).

The effect of oxidation on the behavior of asphaltenes in HVGO has complexities in the conflicting findings reported in the literature. While some studies have suggested that oxidation can increase the concentration and size of asphaltenes, which ultimately alters

the physical and chemical properties such as viscosity (S. Choi et al., 2016; Strelets & Ilyin, 2021b), others have found that it has little or no effect on their behavior (Shojaati et al., 2017). Ultimately, the behavior of asphaltenes in oxidized HVGO will depend on a variety of factors, including the severity and duration of the oxidation, the composition of the HVGO, and the presence of other chemical species (Pu et al., 2020; Shuai Zhao et al., 2020). It is important to consider these factors when assessing the impact of oxidation on the properties of HVGO. In this study, it was discovered that when HVGO was oxidized at high temperatures, heavier products became more abundant unlike in the feed. These heavier solids then formed a gel-like structure leading to a more viscous fluid due to intensive cross-linking (D. Liu et al., 2018; Tannous & de Klerk, 2019).

Additionally, the oxidation process can also cause the formation of other complex molecules, such as resins, that can contribute to the increase in viscosity. While it is true that some double bonds can be relatively weak and more reactive than single bonds, others can be quite strong and stable. The strength of a covalent bond depends on a variety of factors, including the types of atoms involved, the geometry of the bond, and the presence of other functional groups or neighboring atoms that can affect bond strength (Boukir et al., 2001; Serban C. Moldoveanu, 2005).

In the context of the formation of resins during the oxidation of hydrocarbons, indeed, the formation of double bonds between carbon atoms in oxidized molecules can lead to the formation of larger, more complex molecules. This is because double bonds can provide additional sites for polymerization reactions to occur, leading to the formation of longer chains of hydrocarbon molecules. Single covalent bonds could also participate in these reactions, the presence of double bonds could contribute to the overall complexity and

diversity of the molecules that were formed. It is further believed that these molecules could react with asphaltenes to form even larger, more complex molecules that further contributed to the overall higher viscosity of the products, a process termed cross-linking polymerization (Ingold, 1967; Kim, 2021; D. Liu et al., 2018; Siddiquee & De Klerk, 2015).

4.1.2 Volatility Differences

The thermal and time effects on volatility of various samples were analyzed as shown through Figures 15–16 when oxidized accordingly by air and nitrogen - in a period of 4–24 h accordingly. Noteworthy, Figure 15 depicts a larger curvature separation when the temperatures of autoxidation and time spent were both higher. Autoxidized HVGO is known to be containing very strong covalent (C–C or C–H) and hydroxyl bonds (O–H) that ultimately reduce their volatility. The absence or reduction of such bonds leads to higher volatile compounds. Further, addition (heavy) products do contribute highly to the overall nonvolatility.

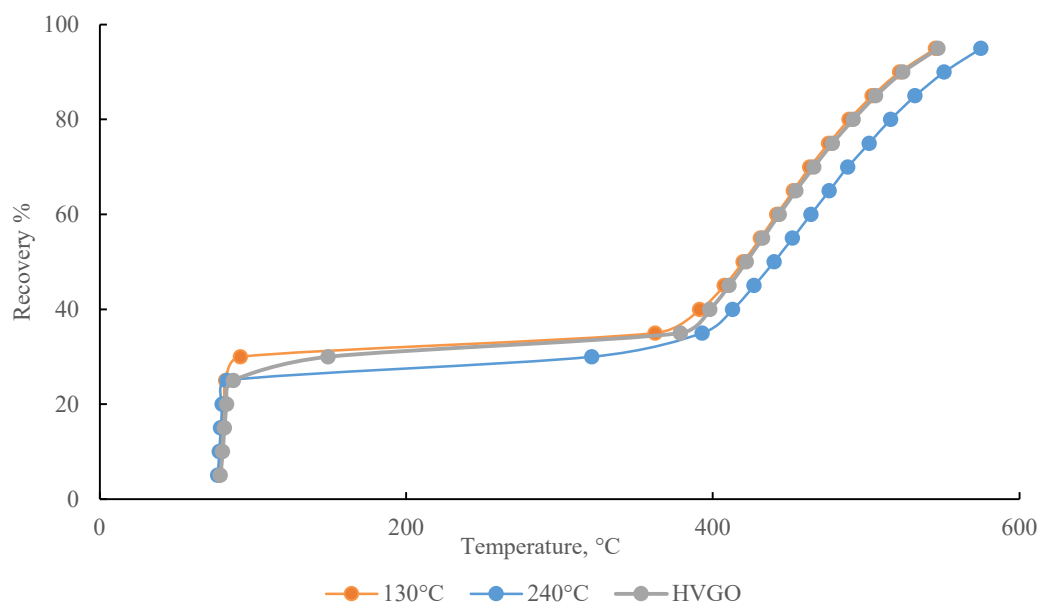


Figure 15 B.P. ranges for samples oxidized by air at 130 °C and 240 °C in 24 h.

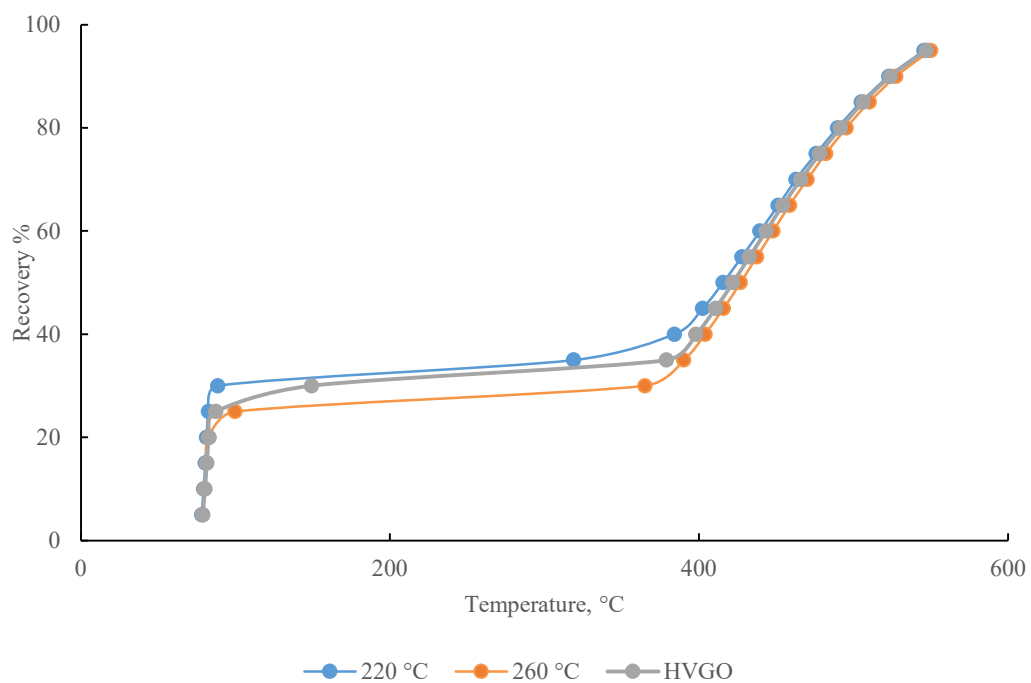


Figure 16 B.P. ranges for samples oxidized by air at 220 °C and 260 °C in 4 h.

A similar or almost a minute difference is noted in Figure 16 when temperatures of autoxidation under 4 h are raised from 220 to 260 °C, suggesting that the effect of temperature increment under the same duration is not quite considerable.

However, the distinction was evident when the time effect was induced in the oxidation process as illustrated by the results in Figure 17. Allowing a longer period of autoxidation proved to result in a highly non-volatile heavy product as its recovery seen in Figure 16 was less than that sample which underwent less reaction time. A longer reaction time did lead to the formation of larger molecules (more complex large products). A similar example is in polymerization reactions; longer reaction times can result in longer polymer chains, leading to a heavier final product (Tannous & de Klerk, 2019).

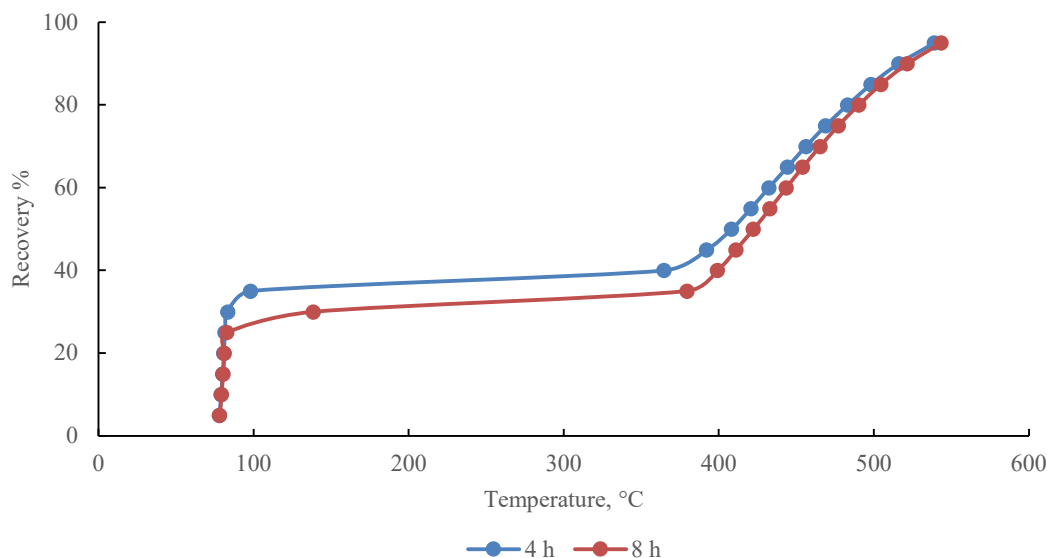


Figure 17 B.P. ranges for samples oxidized through blowing air at 260 °C in 4–8 h.

4.1.3 Improvement in Aromaticity

The aliphatic hydrogen was anticipated to have been replaced by their corresponding aromatic by the formation of more aromatic rings which were expected to have their transmittance at wavelengths of about 1500–1600 cm^{-1} and 3000–3300 cm^{-1} as shown in Figure 18.

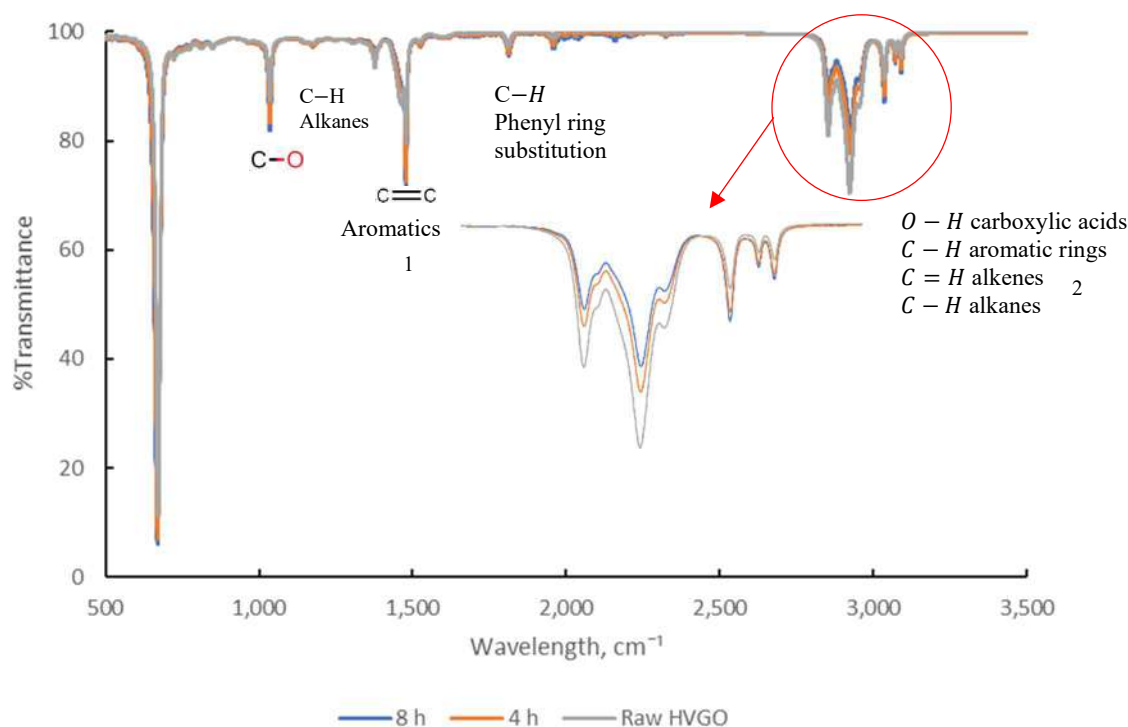


Figure 18 FTIR spectrum for oxidized HVGO by air at 200 °C but different duration

The functional groups that had changed as shown on the spectra of Figure 18 are falling under the stretch of wavelengths of $1000\text{--}1260\text{ cm}^{-1}$, $1500\text{--}1600\text{ cm}^{-1}$, $1600\text{--}2000\text{ cm}^{-1}$, $2850\text{--}2960\text{ cm}^{-1}$ and $2500\text{--}3100\text{ cm}^{-1}$, which matches to C – O, C = C, C – H, C – H, C – H and O – H, C – H, C = H respectively, and their compound type as shown on the figure (Silverstein et al., 2005). Figure 18 displays a very small change in transmittance in the sample that was oxidized in 8 hours than that of 4 hours at the same temperature. This means that the effect of time doubling at such low temperatures gave slight increment results. Positively, both of those samples had aromaticity higher than that of raw HVGO in the stretch of $3000\text{--}3100\text{ cm}^{-1}$.

In order to further comprehend Figure 18, the differences observed in the peaks over the stretches just mentioned, for the change in concentration of the main functional groups

under scrutiny, Figure 19 was generated to clearly depict the enhancement by autoxidation. The higher the percent transmittance shown corresponded to lower concentration of that particular functional group in that sample under those specified operating conditions. For instance, samples autoxidized under 8 h showed higher concentration in aromatics-1 and -2, lower percent transmittance, and showed higher percent transmittance in alkanes which translated to lower concentrations. Hence, increase in time enhanced autoxidation of HVGO by raising their aromaticity, and reduced ultimately their aliphaticity. This finding was also supported by the data obtained from Table 9.

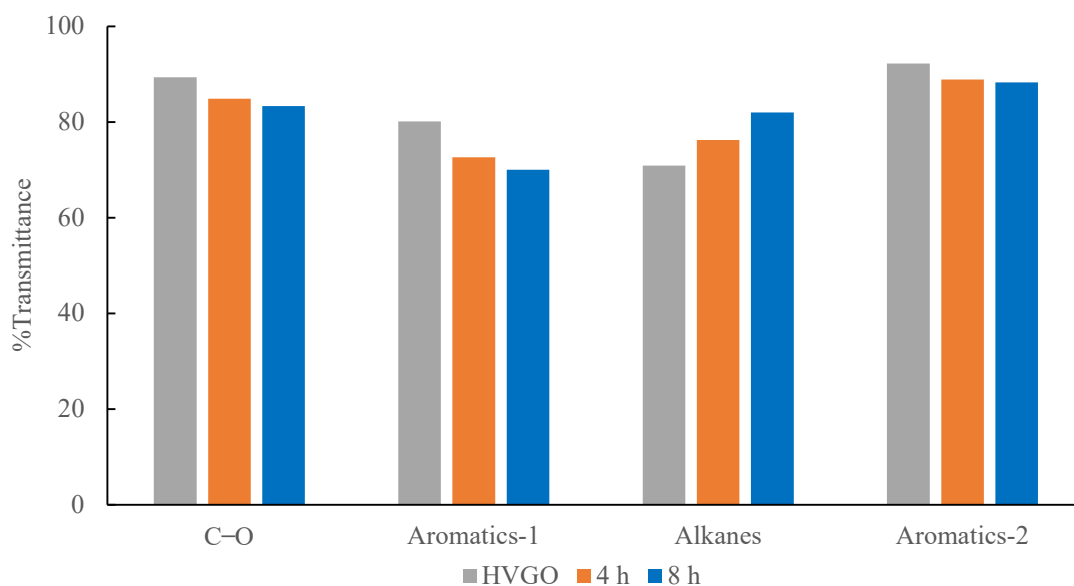


Figure 19 Aromaticity and aliphaticity changes by autoxidation in 4 and 8 h samples

Now, combining the above samples of different temperatures but same time, to study thermal effect, a difference was observed in certain oxidation temperatures. Particularly, the sample oxidized by air at 220 °C showed lower transmittance in esters and carboxyl, phenyl ring substitution and aromatic groups in the wavelengths of 1000–1260 cm⁻¹ and

1600–2000 cm^{-1} , and 3000–3100 cm^{-1} respectively than the rest of the other samples' peaks, inferring that such functional groups were more present after oxidation in lower transmittance than the other compared samples (*Figure 20*). It was possible to observe a lower transmittance for the oxidized sample due to the changes in the chemical composition of the HVGO upon autoxidation (Smith et al., 2008).

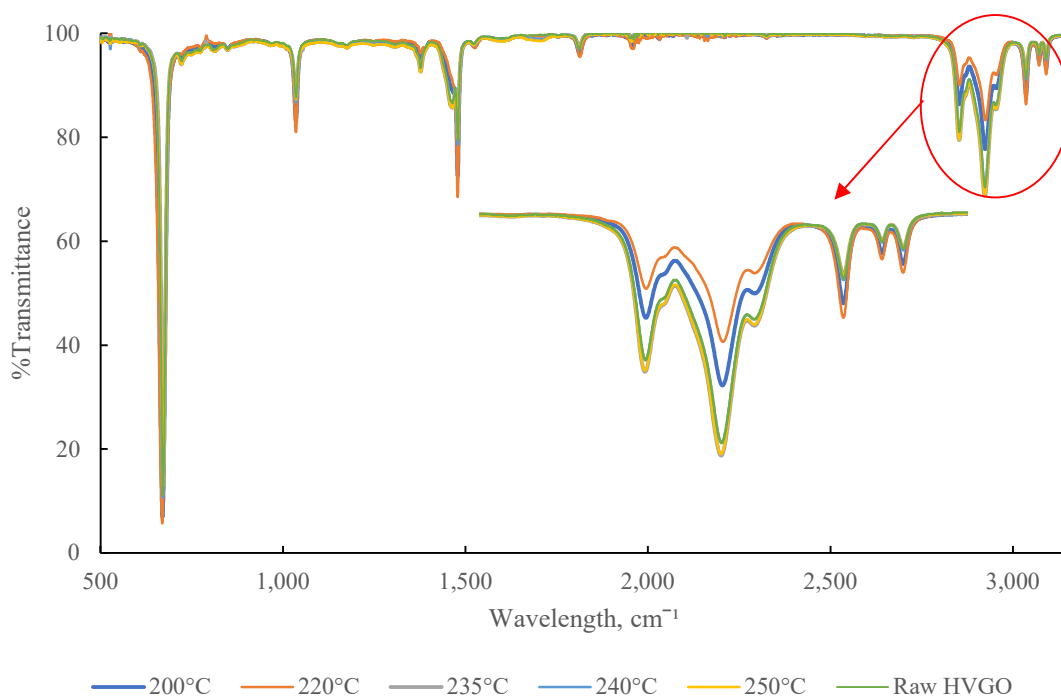


Figure 20 FTIR spectrum for oxidized HVGO at different temperatures in 4 h

Oxidation of HVGO results in the formation of polar compounds such as carboxylic acids and ketones, which are more polar than the hydrocarbons present in the raw HVGO. These polar compounds can dissolve in the solvent used for FTIR analysis and can provide better solubility for the sample in the IR cell. This better solubility and homogeneity of the sample can lead to better contact of the sample with the IR beam and can result in a higher transmittance signal (Kim et al., 2021; Smith et al., 2008).

Additionally, the formation of polar compounds upon oxidation can also lead to changes in the functional groups present in the sample. For example, the presence of carboxylic acid groups can lead to the appearance of a peak in the FTIR spectrum corresponding to the C–O stretch of 1000–1260 cm⁻¹. This peak can contribute to a lower transmittance value in the oxidized sample as compared to the raw sample (Eunkyoung Kim et al., 2011; Silverstein et al., 2005; Smith et al., 2008).

Furthermore, to cement the confirmation of the decrease in aliphatic H from the raw HVGO to the oxidized samples both by nitrogen and air, the results in Table 7 were obtained. Clearly, the decrease in both the ¹H and ¹³C from raw HVGO to either oxidation by nitrogen or air is as a result of the free radical addition to form heavier products which were resulted to a more aromatic alpha base long chain compound (Gao et al., 2022; Li et al., 2015; Montoya Sánchez & de Klerk, 2018; Stratiev et al., 2016).

Table 7 Relative aliphatic and aromatic content in HVGO and oxidized HVGO

Samples	Aliphatic H 0.5–4 ppm	% Reduction	Aliphatic C 0–60 ppm	% Reduction
HVGO	1.89	0	16.08	0
HVGO heated in the presence of N ₂ at 240 °C for 8 h	1.29	32	14.79	08
HVGO heated in the presence of Air at 245 °C for 24 h	1.19	37	11.82	26

4.1.4 Extent of Cross-Linking

In order to study the extent of the cross-linking process due to the autoxidation process by both free-radicals, H-abstraction and conjoining of adjacent molecules, then analyzing the thermal stability of the produced samples was critical as it was believed that highly cross-linked polymers would possess higher thermal stability unlike those less

cross-linked.

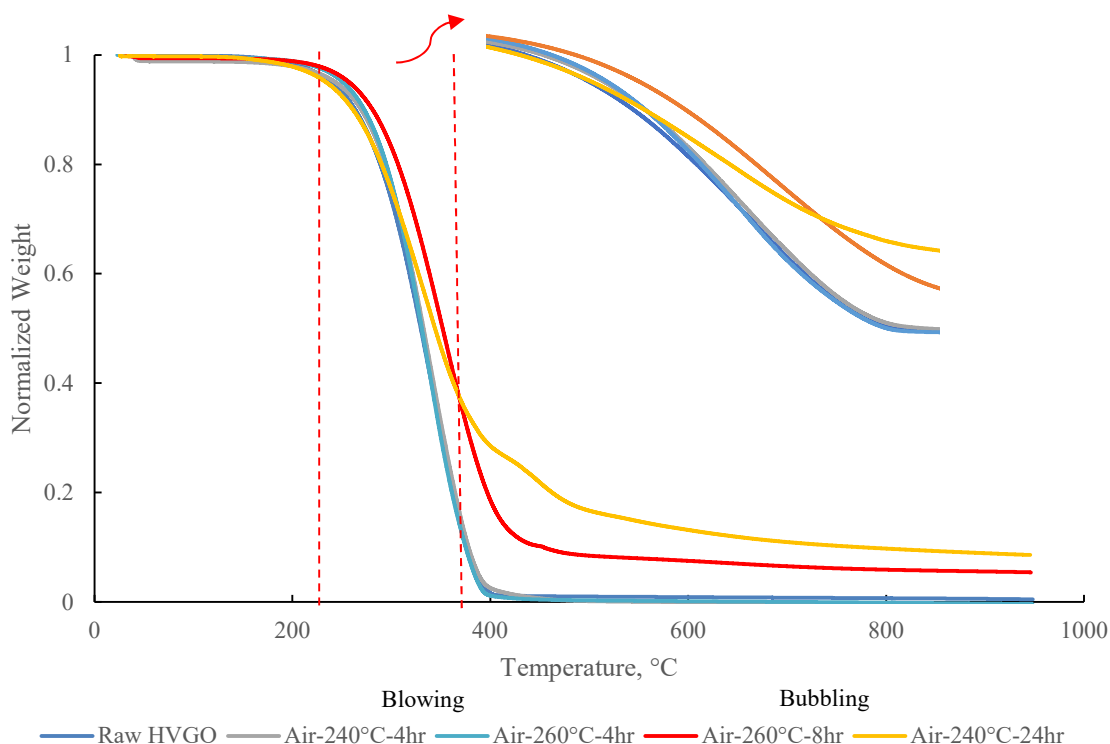


Figure 21 TGA thermograms for raw and oxidized HVGO

It is evident from Figure 21 that an increase in temperature in the oxidation process alters the thermal stability of the samples. For example, oxidized HVGO samples blowing air at 240 °C and 260 °C for 4 h had the highest weight rate loss (less thermal stable) compared to the rest of the samples. At about 450 °C, their TGA residue was almost absent unlike those at longer hours of 8–24 h, it is seen that at 950 °C with about 0.1 normalized residue was present due to higher C that could not be phased out in the temperature range. However, that of 260 °C displayed a higher value than at 240 °C for the reasons the of presence of heavier products as earlier highlighted.

Firstly, the oxidation of HVGO leads to the increase in addition products and additional concentration of polar compounds that affected the thermal stability and

decomposition behavior of the sample. These polar compounds may have lowered decomposition temperatures than the hydrocarbons present in the raw HVGO. As a result, the TGA thermogram for the oxidized HVGO showed a different weight loss profile and decomposition behavior compared to the raw (Chand et al., 2019; Rodgers & McKenna, 2011).

Secondly, the amount and type of polar compounds formed during the oxidation process may vary depending on the oxidation conditions such as temperature, time, and the presence of oxygen. For instance, higher oxidation temperatures and longer oxidation times are believed to have led to the formation of more polar compounds, which caused the TGA thermogram for the oxidized HVGO to show different values at different temperatures (James G. Speight, 2014; Rodgers & McKenna, 2011; Strausz & Lown, 2003).

Moreover, the presence of different functional groups in the polar compounds formed upon oxidation could also have affected the thermal stability and decomposition behavior of the oil. For example, carboxylic acids, which are commonly formed during the oxidation of HVGO, may have decomposed at different temperatures depending on the type and structure of the acid. This caused the TGA thermograms for the oxidized HVGO to show different values at different temperatures (Hong BASc, 1991).

4.1.5 Softening Point Changes

Softening points of some products samples were compared with the raw HVGO and the results were over satisfactory and astonishing (Table 8). Corresponding viscosity

data were also reported in Table 8. The highest softening point was of those samples oxidized at longer periods and elevated temperatures, at over 200 °C.

Table 8 Softening point data recorded for oxidized HVGO samples-thermal and time effect.

Material and operating conditions	Softening Point, °C	Viscosity, cP
Raw HVGO	37.2	729.6±129
Oxidized HVGO by bubbling and mixing air at 240 °C, 24 h	126.6	1919.1±220
¹ Oxidized HVGO by bubbling and mixing air at 260 °C, 8 h	>200	1543.3±252
¹ Oxidized HVGO by blowing air at 200 °C, 24 h	>200	1586.6±257
² Oxidized HVGO by bubbling and mixing N ₂ at 240 °C, 8 h	93.6	1048.7±187

¹The equipment used was programmed to measure until 200 °C by use of glycerin media. ²For control purposes.

The increment in softening point is believed to be attributed by the highly cross-linked compound because of addition products. The intensive long chain did lead to very thick and viscous products compared to non-oxidized HVGO; which was rather softer and wax-like. The inter-linked rings required higher temperatures to soften unlike simple structures present in the raw, thus, a highly increased value of softening point was recorded (Alcaniz-Monge et al., 1997; Barr & Lewis, 1978; Kim et al., 2021; Maeda et al., 1993).

The softening point of oxidized HVGO is an important property for CF production as it affects the thermal stability of the resulting CFs. Carbon fibers are typically produced by heating precursor materials to high temperatures in the absence of oxygen, which causes the material to decompose and form a carbonaceous solid (Frank et al., 2012; Park, 2015). The softening point of the precursor material is an important factor as it determines the temperature at which the material will soften and deform, which can affect the quality of

the resulting carbon fibers (Alcaniz-Monge et al., 1997; Hiremath et al., 2017; Jana et al., 2022).

An increase in the softening point of the oxidized HVGO would be beneficial for CF production as it would allow for higher temperature processing without softening or deformation of the precursor material. This would potentially result in CFs with improved thermal and mechanical properties (Alcaniz-Monge et al., 1997; Kim et al., 2021; Maeda et al., 1993; Tadayuki Matsumoto & Mochida, 1992).

4.2 Effect of Partial Pressure of Oxygen

This section aimed to investigate the role of partial pressure of oxygen (taking advantage of ~21% oxygen in the air) to autoxidize samples of HVGO and examined the extent of such reaction compared to 0% oxygen (by use of nitrogen). The same operating conditions were used accordingly, and results provided. It should rather be emphasized that this study specifically targeted to examine the possibility of controlled autoxidation under anoxic conditions and the consequential findings presented in this research.

4.2.1 Changes in Viscosity

The effect of utilizing oxygen gas in air in autoxidation reaction affects the flow movement of the samples eventually. While nitrogen gas was used as an inert (and as control), its 100% concentration limited any presence of oxygen during its purging.

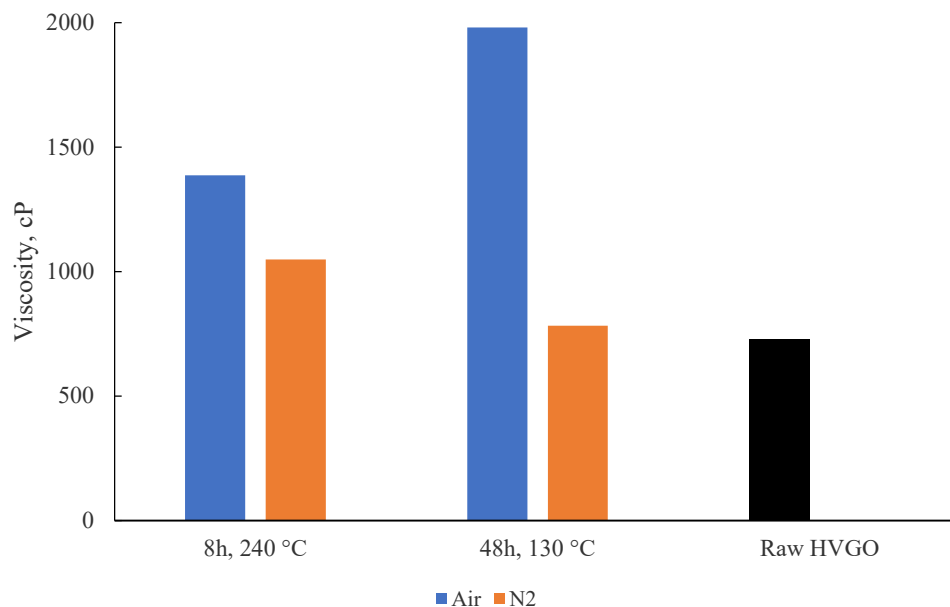


Figure 22 Viscosity values for the oxidized samples by bubbling and mixing at different temperatures and times.

Most of the samples exhibited the expected results of increasing viscosity with increasing reaction temperatures. This is as a result specific fluids tend to thicken when temperature is raised. However, in a few cases, some products obtained, showed a slight increase in viscosity than raw HVGO as depicted in Figure 22, for example, the sample heated in the presence of N_2 at 130 °C in 48 h had a viscosity of 782.8 cP. The viscosity of heavy oil increased with reaction temperature because increasing the temperature increases the kinetic energy of the molecules in the oil, causing them to move more rapidly and leading to higher yield by enabling more functional groups to cross-link and conjoin

between them. As a result, the oil becomes more viscous and flows less easily (Chukwu & Ezugwu, 2018; James G. Speight, 2014; Kurt Konhauser, 2006).

It is important to note that the relationship between temperature and viscosity is not linear, and that there is a point at which increasing the temperature may actually increase the viscosity again due to changes in the oil's chemical composition or other factors. However, for many heavy oils, increasing the temperature will generally reduce viscosity and make the oil easier to transport and refine (ASTM International, 2022; Encyclopedia Britannica, 2022; James G. Speight, 2014).

4.2.2 Volatility Differences

As seen in Section 4.1.2, the change in volatility is investigated here for the effect of partial pressure of oxygen. The heavy product formation by the presence of free radicals has been examined to check if that was viable.

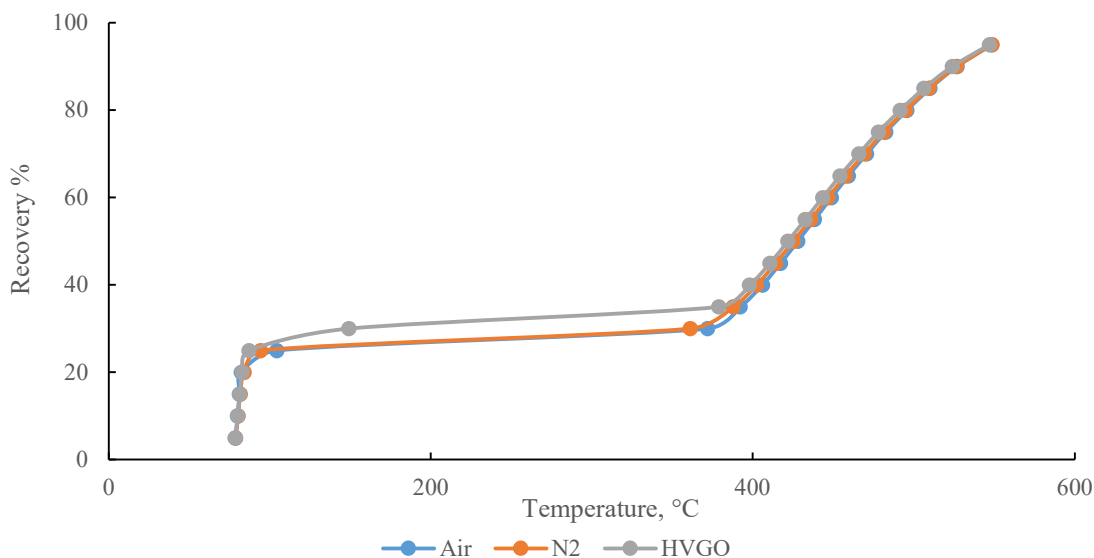


Figure 23 B.P. ranges for samples oxidized through blowing air or N2 at 200 °C in 4 h.

It is observed that there are no significant changes in boiling point ranges when HVGO samples are oxidized by air or nitrogen under the same temperature and duration as depicted in Figure 23. In the case of the samples of oxidized HVGO, the ones oxidized by air and the others by nitrogen gas, the gap in the results can be attributed to differences in the oxidation products formed under these two conditions. While the distribution of free radicals in the oil may have contributed to the observed reduction in viscosity of the samples, it is important to note that other factors such as the experimental temperature and processing conditions may have also played a role in shaping the boiling point distribution curves (Barr & Lewis, 1978; Tannous & de Klerk, 2019).

But when HVGO is oxidized by air, it undergoes autooxidation, where both the unsaturated hydrocarbons and saturated (C–H) in the oil react with oxygen in the air to form oxidized products such as ketones, alcohols, and carboxylic acids (Montoya Sánchez & de Klerk, 2018). These products have higher boiling points than the original hydrocarbons, which can result in a shift in the boiling point distribution curve to higher temperatures (Bojkovic et al., 2021). From Figure 24, the differences in temperature ranges noted were quite small between the oxidation by air and nitrogen as the control; the air being less volatile as from 40–95% recovery.

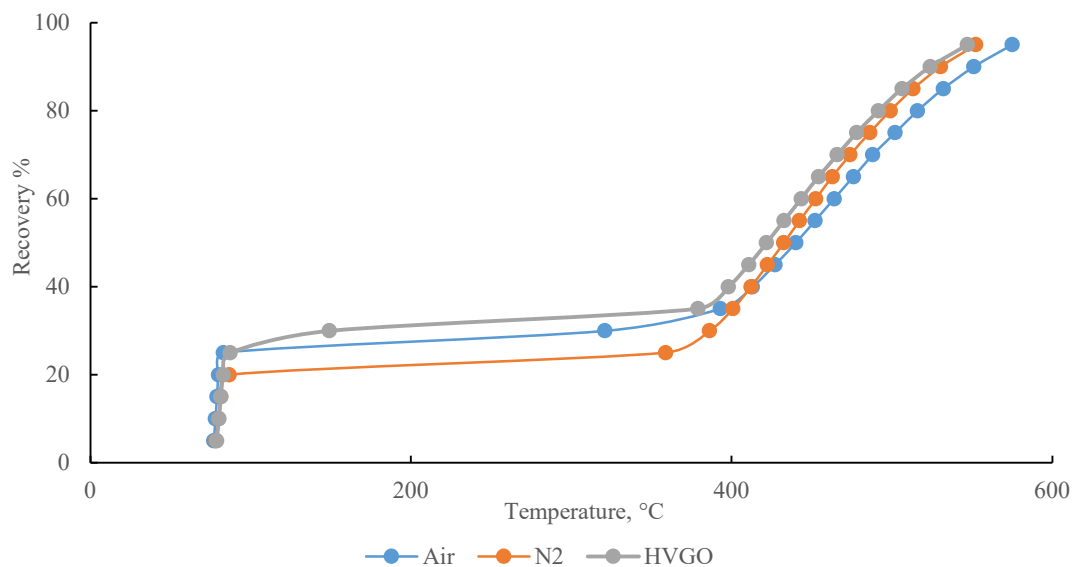


Figure 24 B.P. ranges for samples oxidized by air and nitrogen at 130 °C in 24 h.

4.2.3 Improvement in Aromaticity

Aromatic rings play a huge role in the stability of very strong compounds formed.

Aromatics are expected to form when partial pressure of oxygen is controlled.

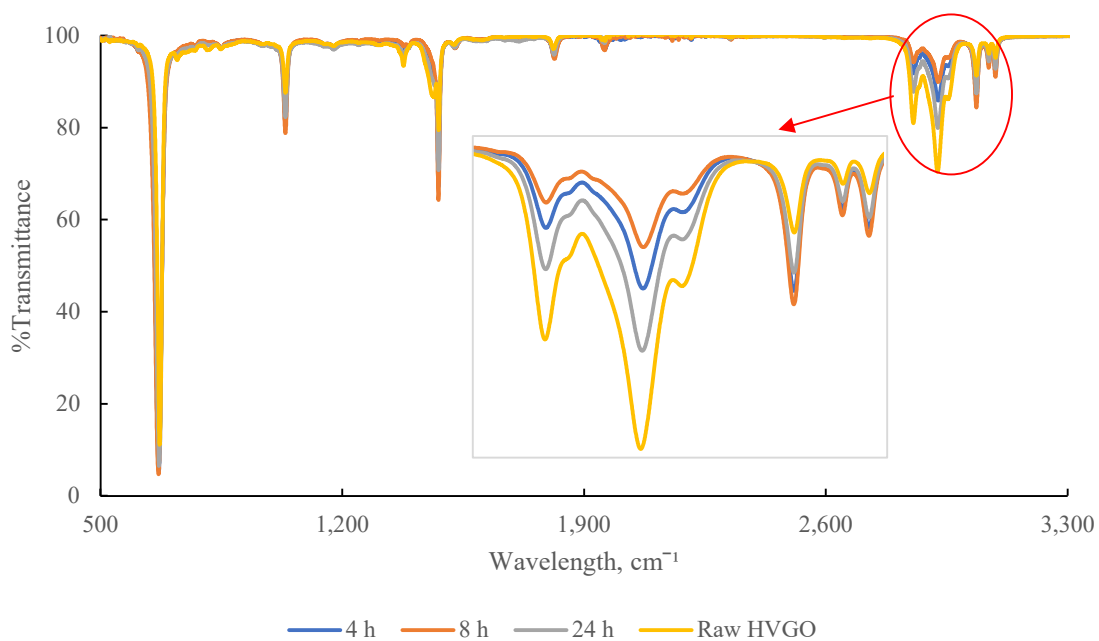


Figure 25 FTIR spectrum for oxidized HVGO by blowing air at 200 °C but different durations.

Once again, it can be observed from Figure 25 that the functional groups that had changes are on the stretch of wavelengths of $1000\text{--}1260\text{ cm}^{-1}$, $1500\text{--}1600\text{ cm}^{-1}$, and $2500\text{--}3100\text{ cm}^{-1}$, which corresponds to $C-O$, $C=C$ and $O-H, C-H, C=H$ respectively, and their compound type as earlier shown in the Figure 18 (Silverstein et al., 2005). From Figures 25 and 26, it is also noted that there is a clear change in the aromatic rings around the wavelengths $2500\text{--}3100\text{ cm}^{-1}$ concerning their concentration when thermal and time effects are studied. Blowing air is characterized by limiting mass transfer for effective autoxidation process. At 8 h, it showed the highest changes (lowest transmittance in aromatic rings stretch) in aromaticity, inferring that it was the most effective duration for blowing air at specifically $200\text{ }^{\circ}\text{C}$.

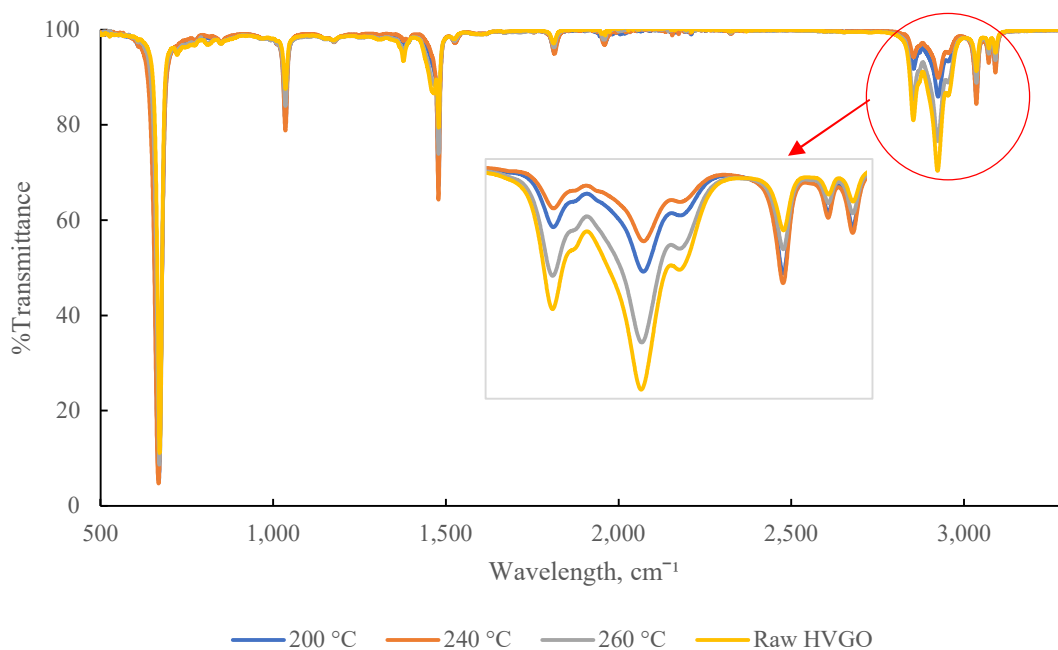


Figure 26 FTIR spectrum for oxidized HVGO by blowing air at different temperatures in 4 h

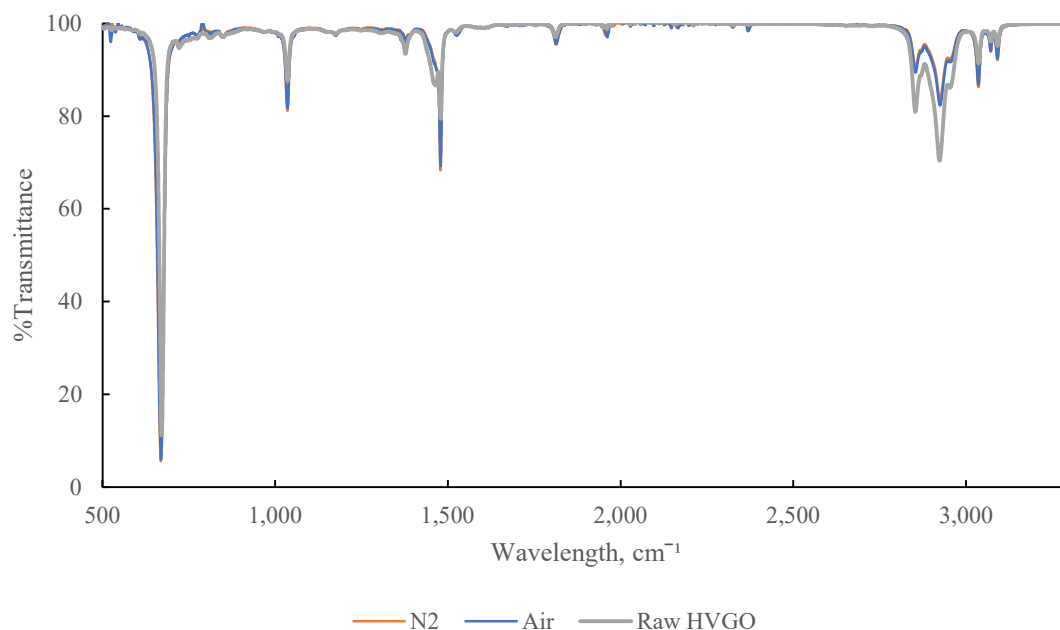


Figure 27 FTIR spectrum for oxidized HVGO by air and N₂ for 4 h and 240 °C

However, Figure 27 clarifies the concept that exposure of the samples to air or nitrogen for a duration of four hours had a negligible effect on autoxidation. This suggests that short-term autoxidation by blowing using either air or nitrogen gas does not result in significant variations in the resulting properties of the samples. The sole noteworthy differences were observed under the distinct operating conditions that were previously identified, higher temperatures and longer periods. Although both had shown changes in aromaticity from raw HVGO under the stretch of 2500–3100 cm⁻¹.

4.2.4 Extent of Cross-Linking

The experimental approach was designed to minimize variability and ensure reproducibility, and the repeated results consistently demonstrated the ability to detect even

minor changes in thermal stability with a high degree of precision. While it is important to continue to validate the findings through further replication, the evidence suggests that the analytical approach is sensitive and reliable as demonstrated in the next results below. Now, the thermal stability of oxidized samples was analyzed to examine the effect of partial pressure of oxygen under certain conditions as depicted in Figures 28 and 29 when either blown or bubbled.

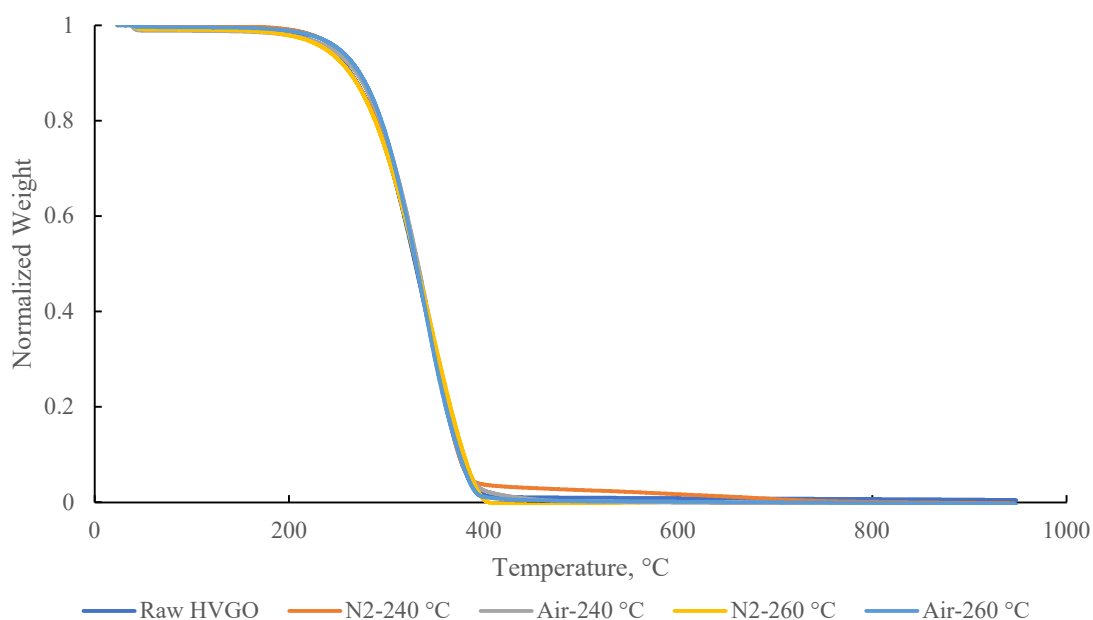


Figure 28 TGA thermograms for raw and oxidized HVGO in 4 h-by blowing.

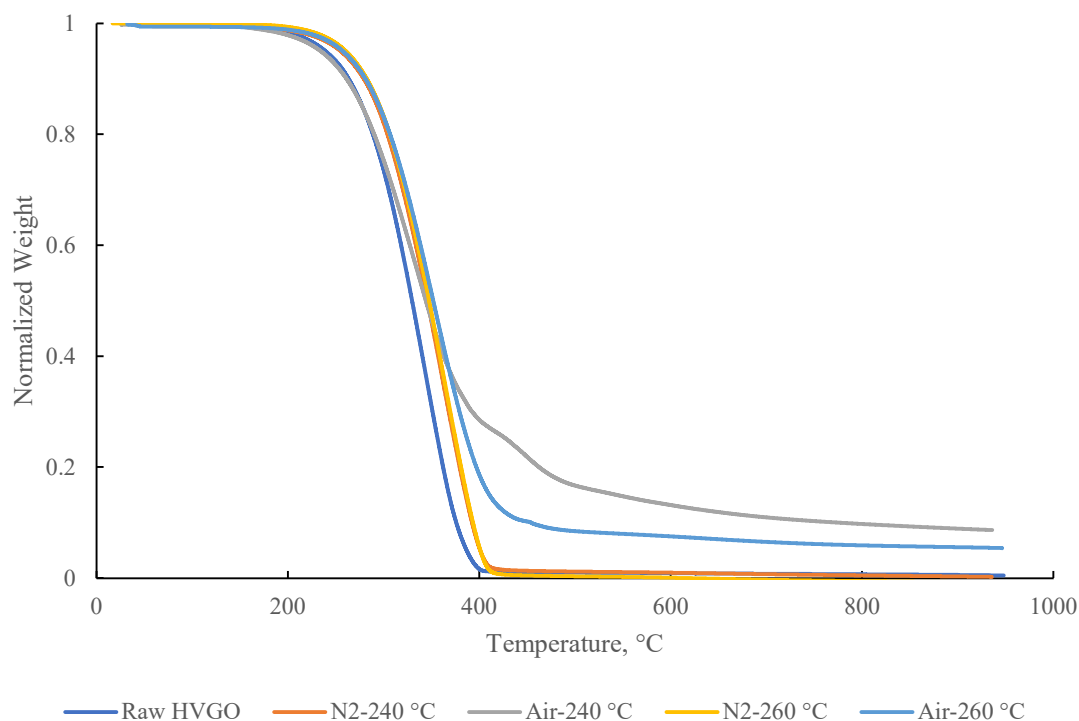


Figure 29 TGA thermograms for raw and oxidized HVGO in 4 h-by bubbling and mixing.

Increase in autoxidation temperature results in a similar weight loss rate for the air and nitrogen blowing as shown in Figure 28. This trend is believed to be because of the mass transfer limitation from the liquid surface to bottom of the reactor. However, the presence of more volatile components and free radicals when either oxidized by air or nitrogen, respectively, at elevated temperatures resulted in higher weight loss than when thermal stability check was analyzed. However, when comparison was made between the blowing and bubbling effects, those of bubbling had a wider range curvature than those of blowing as depicted in Figure 29, that is, difference in slopes. It should be noted that the samples compared were from 240–260 °C in order to see clearly the extent of such study, which is examination of partial pressure of oxygen on the oxidation extent.

4.2.5 Softening Point Changes

Similarly, to check how partial pressure of oxygen played a role in altering the softening point of the oxidized samples, the following were the results obtained. It is evident that at the given analyzed conditions, autoxidizing by air has a more increment compared to nitrogen, however both have appreciable change of over ~200% as shown in Table 9. It also reports corresponding viscosities.

Table 9 Softening point data recorded for oxidized HVGO samples- partial pressure of oxygen.

Material and operating conditions	Softening Point, °C	Viscosity, cP
Raw HVGO	37.2	729.6±129
Oxidized HVGO by bubbling and mixing air at 240 °C	126.6	1919.1±220
Oxidized HVGO by bubbling and mixing N_2 at 240 °C	93.6	1048.7±187

4.3 Effect of Mixing and Gas-Liquid Interfacial Area

4.3.1 Changes in Viscosity

To determine if the bubbling and blowing of gases had any effect in autoxidation reaction, specific properties of product samples were investigated, and their results were shown and elaborated here. It is critical to note that the mass transfer of fluid may be affected by several factors, namely film thickness, temperature, agitation, state of material, time and surface area to volume ratio. In this study, specifically focused on bubbling (or blowing) air (or nitrogen) and the use or absence of a magnetic stirrer. A few properties under examination for CF precursor suitability were viscosity, volatility, thermal stability, and aromaticity as shown herein.

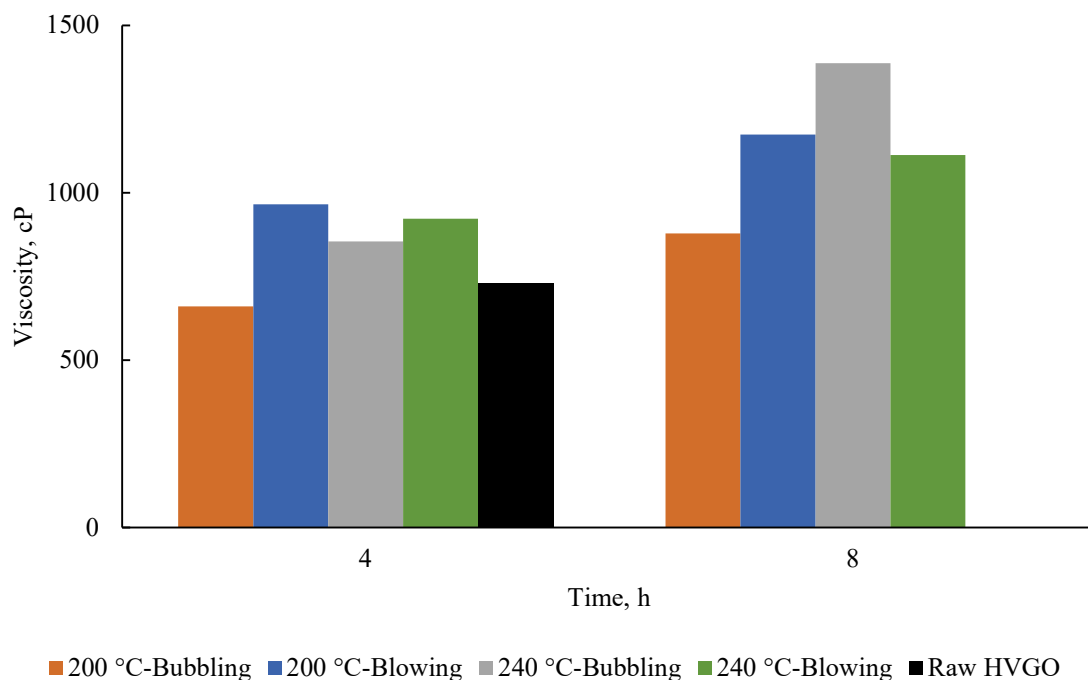


Figure 30 Viscosity differences between oxidized samples by air through bubbling and blowing against time.

To study the distinct differences between bubbling and blowing of air through and over the HVGO samples, Figure 30 displays the viscosity changes as a result of the effect of the rigorous air mixing and just blowing over. Each increase in temperature and time showed an increment in viscosity, for example, bubbling at 200 °C in 4 h had a viscosity of 660.7 cP while doubling the time to 8 h, its viscosity increased to 878.5 cP. However, when comparing at same time but different air injection, for example at 4 h and 200 °C, it is observed that, blowing air had a higher viscosity of 964.9 cP than that of bubbling and mixing. It would be worth to note, for the samples under study here, the highest from Figure 30 was that of bubbling and mixing air for 8 h at 240 °C with a viscosity of 1386.6 cP.

Bubbling and mixing air into HVGO could have higher autoxidation effects than just blowing air in certain conditions because of the increased surface area of the HVGO that is exposed to oxygen (in the air). When air is bubbled into HVGO, it creates small bubbles

that increase the contact area between the HVGO and air. This increased contact area allows for a greater amount of oxygen to come into contact with the feed, which can promote more rapid oxidation (Houda et al., 2018; Kim et al., 2021; Montoya Sánchez & de Klerk, 2018).

In contrast, when air is simply blown over the surface of the oil, there is less contact between the oxygen and the oil, and therefore less opportunity for oxidation to occur. This is because the air can only react with the HVGO at the surface, and as the surface area is limited, the reaction is slower (Houda et al., 2018). Additionally, bubbling and mixing air into HVGO could also increase the mixing of the reactants, which helped distribute the oxygen more evenly throughout the feed. This could further promote oxidation and increase the autoxidation effects (Bouaifi et al., 2001; Sato, 2014; Siddiquee, 2016).

However, the limited oxygen supply in blowing did show higher values like those samples at 200–240 °C in 4 h due to control of the amount or concentration of oxygen reaching the entire feed inside the flask. This limited control resulted in an even higher concentration of heavier products as could be predicted by the autoxidation reaction pathway in Section 2.3.

While also examining the effect of partial pressure of oxygen, some samples were heated in the presence of N_2 and their results were analyzed as shown on Figure 31. The majority of the samples had higher viscosity than the raw HVGO with the highest value recorded at 1059.6 cP which was heated by blowing N_2 at 240 °C in 8 h. Blowing in 8 h and at 240 °C had a higher viscosity than those bubbled and mixed at similar condition as a result of more control and product selectivity as inferred by the reaction pathway in

Section 2.3. The presence of free radicals and further formation of them at elevated temperatures did lead to more ring-closure and addition products which contributed to higher viscosities (Chukwu & Ezugwu, 2018; Kim et al., 2021).

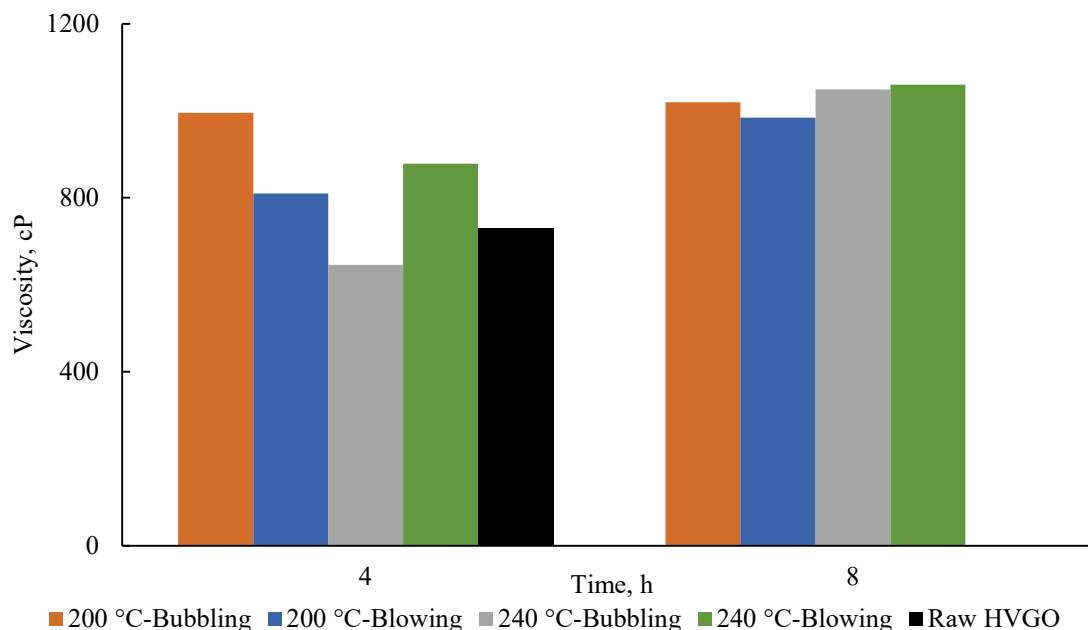


Figure 31 Viscosity values for the oxidized samples under bubbling and blowing N₂ in different temperatures and times.

4.3.2 Volatility Differences

It is quite worth noting that in Figure 32, when the samples heated at 200 °C through 8 hours by bubbling and blowing air, the gap between 20–40% recovery is quite significant. However, the final temperatures tend to merge as the recovery goes to 95%. The high molecular weight, more viscous and addition products attributed to bubbling air showed a lower recovery rate at the same temperature than those blown; this indicates their lower volatility compared to the air-blown samples (Houda et al., 2018; Mao et al., 2020; Tannous & de Klerk, 2019). The difference in volatility would be due to the change in a

chemical structure having stronger covalent, hydroxyl, and hydrogen bonds collectively in the bubbled than those in the blown product samples, thus, different percent recoveries at a particular temperature (Kotti et al., 2009; Mao et al., 2020).

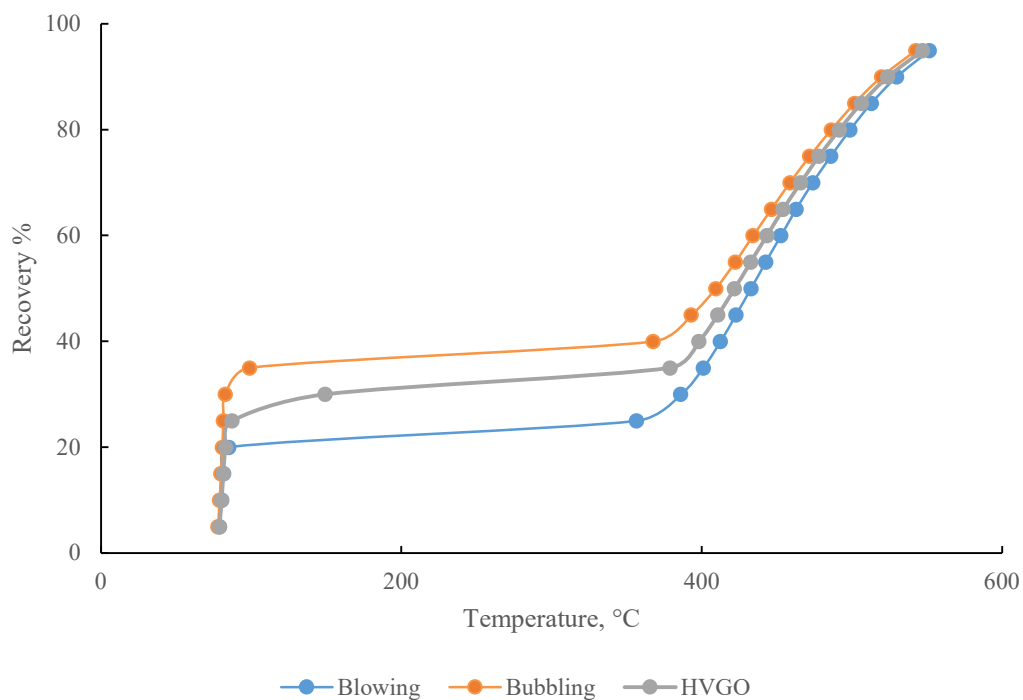


Figure 32 B.P. ranges for samples oxidized by air at 200 °C in 8 h through bubbling and blowing.

4.3.3 Extent of Cross-Linking

Now, when studying the effect of mixing and G-L interfacial area on the thermal stability of the oxidized samples, the following results were obtained.

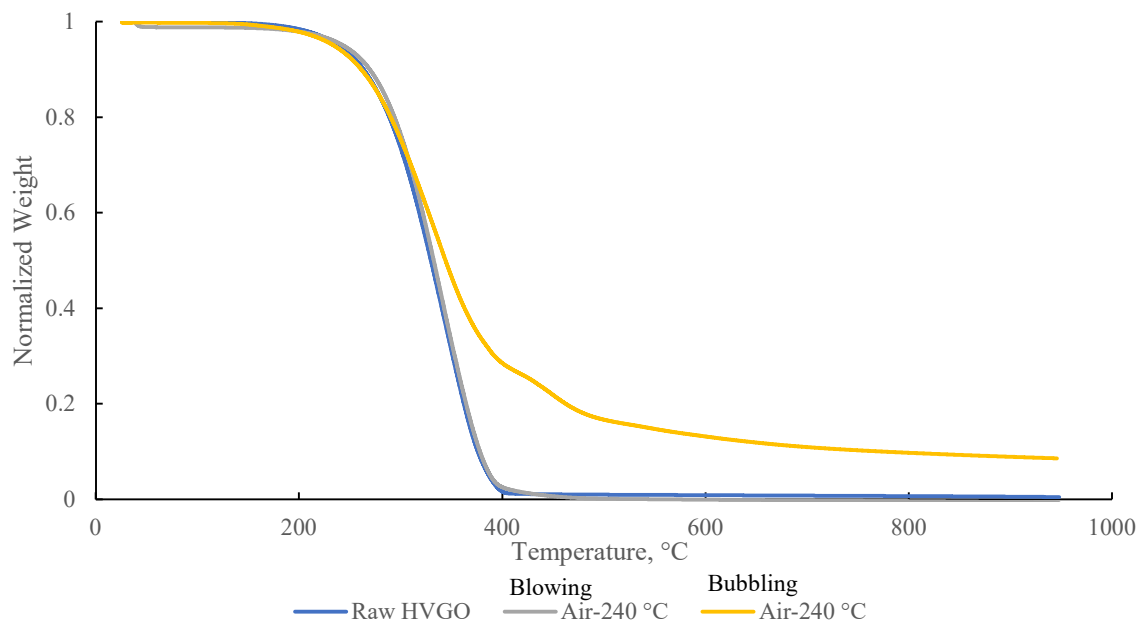


Figure 33 TGA thermograms for raw and oxidized HVGO in 4 h-by bubbling and blowing.

Blowing air for low durations such as 4 h and 240 °C has shown a little deviation from the raw HVGO, unlike that sample where it was bubbled under the same conditions as demonstrated in Figure 33. However, that deviation was noticed to be larger for the TGA residue after 450 °C than those bubbled at elevated temperatures and double the time as shown in Figure 34.

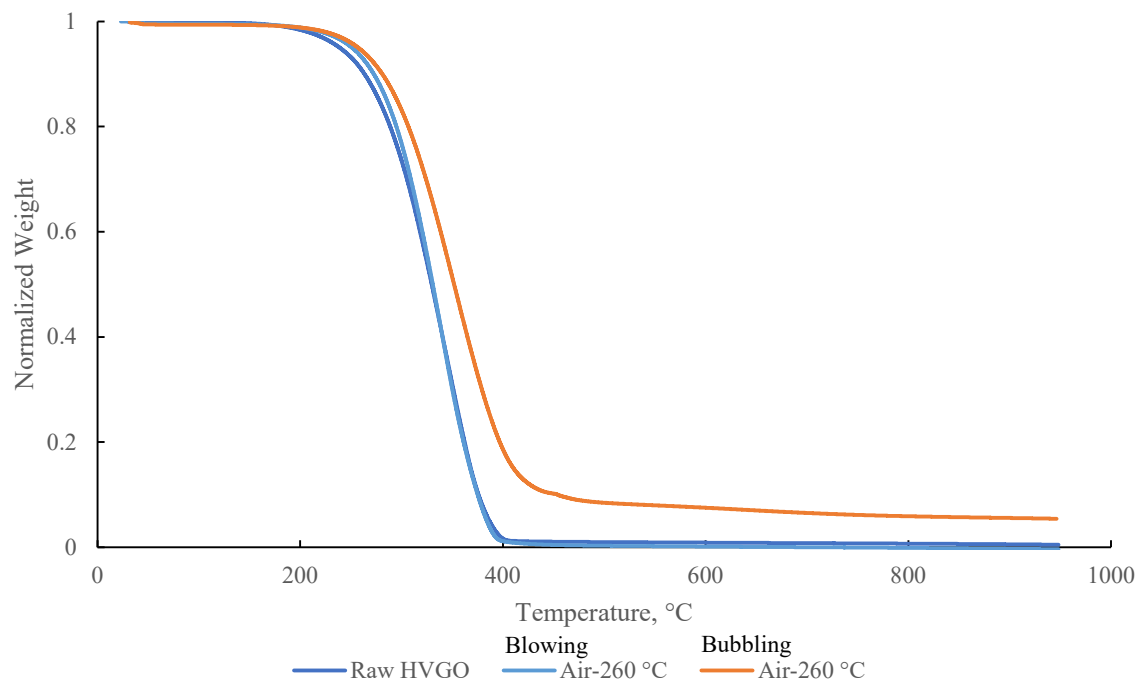


Figure 34 TGA thermograms for raw and oxidized HVGO in 8 h-by bubbling and blowing.

4.3.4 Softening Point Changes

Now, for softening point, it was observed that mixing and G-L interfacial area did play a role in changing the value from raw HVGO as shown in Table 10. Blowing air at 240 °C show a higher increment than bubbling at the same condition. However, both bubbling and blowing air at the elevated temperature and elongated duration resulted in an even more appreciable softening point.

Table 10 Softening point data recorded for oxidized HVGO samples-mixing and G-L interfacial area.

Material and operating conditions	Softening Point, °C	Viscosity, cP
Raw HVGO	37.2	729.6±129
Oxidized HVGO by bubbling and mixing air at 240 °C	126.6	1919.1±220
Oxidized HVGO by blowing air at 240 °C	133.9	1112.5±173
¹ Oxidized HVGO by bubbling and mixing air at 260 °C, 8 h	>200	1543.3±252
¹ Oxidized HVGO by blowing air at 200 °C, 24 h	>200	1586.6±257
Oxidized HVGO by bubbling and mixing N ₂ at 240 °C, 8 h	93.6	1048.7±187

¹The equipment used was programmed to measure until 200 °C by use of glycerin media.

4.4 What is in the Light Components Evaporated in Autoxidation of Heavy Petroleum and what are the Characteristics of Asphaltenes Produced?

The autoxidation of heavy petroleum is a thoroughly studied process to produce high-quality carbon fiber precursors. During this process, the heavy petroleum undergoes a series of chemical reactions that result in the formation of various byproducts. One such byproduct is the light components that are first evaporated during the heating process (James G. Speight, 2014). These components are known to play a crucial role in the formation of asphaltenes, which are a key component of the carbon fiber precursor (Fan et al., 2014; Park, 2015). Understanding the chemical composition of these light components and their role in the formation of asphaltenes is therefore essential for optimizing the autoxidation process and producing high-quality, sustainable carbon fiber precursors (Javadli & de Klerk, 2012; L. Yang & Sheng, 2020).

In addition to the light components evaporated during the autoxidation process, the resulting asphaltenes are another important component of heavy petroleum that are of interest to researchers. Asphaltenes, the complex and polar molecules produced during the autoxidation of heavy petroleum, are important precursors for high-performance carbon fibers (Zuo et al., 2019). The composition and properties of asphaltenes are dependent on various factors, such as the type of heavy petroleum and the conditions used during the autoxidation process. Studying the characteristics of asphaltenes can help us gain insight into their chemical structure and reactivity, which can aid in the optimization of the autoxidation process (Trejo et al., 2004). By understanding the unique characteristics of asphaltenes, researchers can develop efficient and cost-effective methods for producing sustainable and high-quality carbon fiber precursors, which are in high demand for various industrial applications (Frank et al., 2012; Jana et al., 2022; Yokoyama et al., 1979). The data in Table 11 that follows is an example of results obtained from one of the experiments performed and the subsequent FT-IR analysis of the light byproducts.

Table 11 Light components mass balance

Masses before the experiment, g	Mass of products, g	Mass of Light components, g
50.03	46.52	3.51

It can be observed from the FT-IR spectra in Figure 36, the wavelength of several compounds, functional groups, and elements. Firstly, a strong representation of nitro-compounds in the peaks of $1260\text{--}1390\text{ cm}^{-1}$ and $1500\text{--}1660\text{ cm}^{-1}$. Then, light alkanes $C-H$ are observed in the stretches of $1350\text{--}1470\text{ cm}^{-1}$ and $2850\text{--}2960\text{ cm}^{-1}$ (Silverstein et al., 2005). Also, a huge deposition of sulfur is seen (*also* see Table 4 and

Figure 35) in the peaks of 600, 1100 and 1400 cm^{-1} (Cai et al., 2014) and sulfur dioxides in the wavelengths of 500, 1140–1340 cm^{-1} (Bailey et al., 1930).

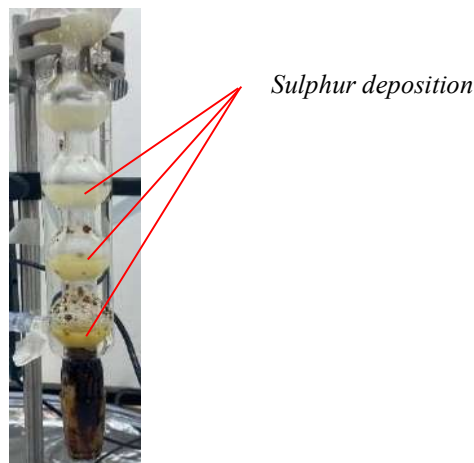


Figure 35 Sulphur deposition inside glass condenser

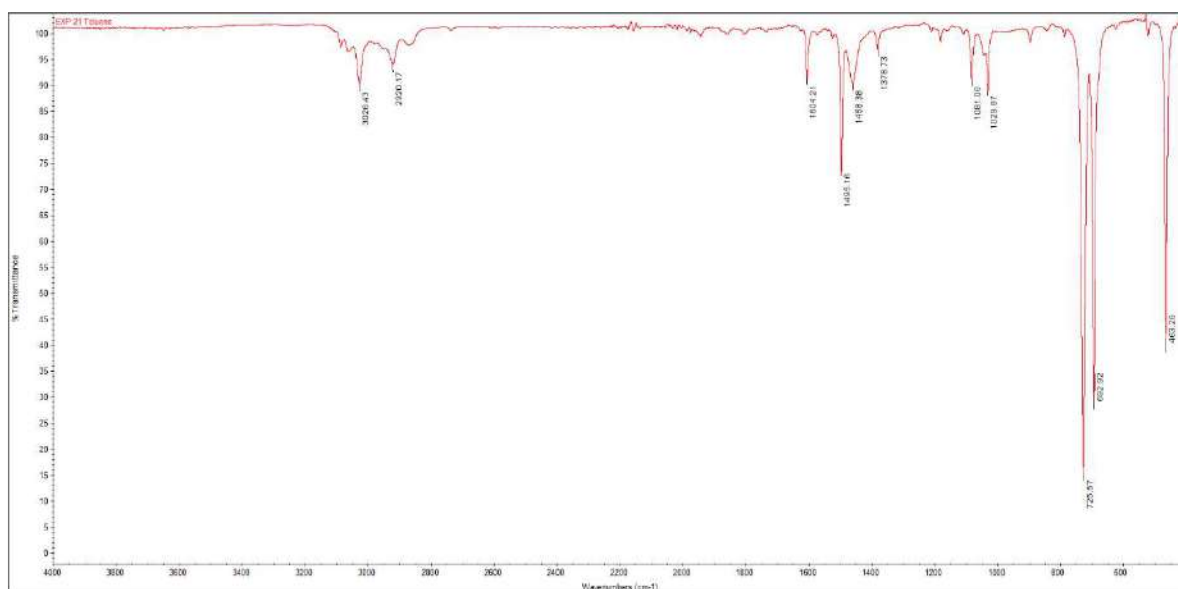


Figure 36 FT-IR spectra for light evaporated products from autoxidized HVGO

Lastly, asphaltenes are typically insoluble in lighter organic solvents, such as pentane, hexane, and heptane, due to their highly complex, branched, and condensed structures. However, they are highly soluble in aromatic solvents, such as toluene, due to the presence of double bonds in their molecular structure (Amjad-Iranagh et al., 2015). The double bonds in the aromatic rings of asphaltenes provide sites for the formation of van der Waals

forces, which promote solubility in aromatic solvents. This solubility was observed when asphaltenes were dissolved in toluene and was found to be part of the aggregate observed after oxidation of HVGO (Buenrostro-Gonzalez et al., 2002). This contributed to the high viscosity in most of the products measured, which can be problematic for industrial processing. The carbon-to-hydrogen ratio of asphaltenes is typically around 1:40, indicating a highly condensed and complex molecular structure (James G. Speight, 2014). Asphaltenes play an important role in the formation of heavy products, as they tend to associate with other heavy molecules and contribute to the high viscosity and density of crude oils (Kim, 2021; Palacio Lozano et al., 2020).

4.5 Suitability of Oxidized Products as Carbon Fiber Precursor

This section presents an elaboration of the obtained results and a comparison with the relevant literature to determine the feasibility of the results for carbon fiber precursor production. After the various quantitative and qualitative analyses, it is evidentiary to mention that there are specific operation autoxidation conditions, temperature, time and mode of air injection, if carefully controlled, then carbon fiber precursors from heavy petroleum such as HVGO studied here can be produced.

Firstly, as shown in Table 12 the obtained results provide compelling evidence that autoxidation of HVGO at temperatures of 130 °C and 220 °C in 8 hours or more, and 240–260 °C for a duration of 4 hours or more, whether by blowing or bubbling air or nitrogen, results in a significant increase in viscosity compared to raw HVGO. The maximum viscosity recorded was about 1979.9 cP, which is approximately 1250 cP higher

than that of raw HVGO. These findings are consistent with earlier studies which have reported an increase in viscosity of the resulting samples compared to the feedstock (García Zapata & De Klerk, 2014; Luo & Gu, 2007).

Secondly, it was noted that to have CF precursors from heavy petroleum, the samples are to have their aromaticity improved considerably through autoxidation. For specific samples, for example autoxidized by bubbling and mixing air at 240 °C for 24 h, its aliphatic H reduced by 37%. Another sample was the one autoxidized at 220 °C for 4 h by bubbling and mixing air. Notwithstanding, some samples that were heated at 240 °C in 8 h in the presence of N_2 had their aromaticity improved noticeably by a reduction of aliphatic H by 32%. These results are validated by previous studies done as shown in Table 12 (D. Liu et al., 2018; Montoya Sánchez & de Klerk, 2018; Stratiev et al., 2016).

Thirdly, CF precursors and CF are supposed to be highly thermal stable compounds to produce very tensile and modulus CFs. In that regard, focusing on one example from Table 12, it was shown that (Aldosari et al., 2021) had improved the thermal stability of the precursors to about 800 °C. Here, it was possible to have a considerable TGA normalized weight residue of about 0.1 even at the maximum device temperature of 950 °C for the sample autoxidized by air for 24 h at 240 °C as shown in Table 12.

Moreover, to ensure that the suitability of certain samples did exhibit the most important property of softening point, it was possible to raise appreciably the softening point by over 400% for certain conditions. For instance, the sample which was oxidized by bubbling and mixing air at 260 °C for 8 h and that which was oxidized by blowing air at 200 °C for 24 h. Besides, it was successful to enhance the softening point by heating HVGO in the presence of N_2 at 240 °C for 8 h resulting to about 115 °C from 37.2 °C of HVGO.

These successful results are evidentiary as from earlier studies as shown in Table 12 (Díez et al., 2012a; Kim, 2021; Kim et al., 2021; Li et al., 2015; D. Liu et al., 2018).

Table 12 Suitability data for produced CF precursors in the study.

Property	Condition	This study	Literature	References
Viscosity	- Bubbling 240–260 °C and 8+ h - Blowing 200–240 °C, 8+ h (air/N₂)	6400+ cP¹ 3400+ cP¹	6357 cP ¹	(Lam-Maldonado et al., 2023)
Volatility	- Bubbling 240–260 °C and 8+ h - Blowing 200–240 °C, 8+ h (air/N₂)	Less Volatile	Not reported	—
Thermal Stability	240 °C, 24 h	950+ °C	800 °C	(Aldosari et al., 2021)
Aromaticity	- Bubbling 240 °C, 24 h air - Blowing 240 °C, 8 h N₂	37% of aliphatic H/C reduction 32% of aliphatic H/C reduction	0.77 aromaticity from CTP - Decrease of aliphatic H	(Banerjee et al., 2021; Maeda et al., 1993)
Softening Point	- Bubbling air at 260 °C for 8 h - Blowing air at 200 °C, 24 h - By N₂ at 240 °C, 8 h	- Over 400% increase >200 °C 115 °C from 37.2 °C	239 °C - Not reported	(Li et al., 2018) -

¹Measured at 25 °C

However, it is inconclusive to highlight at this juncture the type of precursors that will eventually be produced, but as per the obtained results, then High Performance Carbon Fibers (HPCF) are more challenging to be fabricated unlike General-Purpose Carbon Fibers (GPCF). HPCF exhibits exceptional performance in terms of its mechanical properties, such as high tensile strength, high stiffness, and high fatigue resistance. They are typically produced using high-quality precursor materials, such as PAN or pitch, that undergo specialized processing techniques, such as high-temperature pyrolysis and controlled oxidation, to produce CFs with superior performance characteristics. Their

common uses are in high-end applications, such as aerospace, defense, and sporting goods, where the demand for high-performance materials is critical (Alcaniz-Monge et al., 1997; J. Liu et al., 2022; Maeda et al., 1993).

Whereas GPCF is less specialized than HPCF, but still offers good performance characteristics for a wide range of applications. They are typically fabricated using lower-quality precursor materials, like lower-grade PAN or pitch, and undergo simpler processing techniques, for example lower-temperature pyrolysis and less controlled oxidation. The resulting CFs are still high-strength and high-stiffness but may have lower fatigue resistance and other mechanical properties compared to HPCF. GPCF is commonly used in a variety of applications, such as automotive, wind energy, and industrial manufacturing, where the demand for high-performance materials is not as critical as in high-end applications. (Alcaniz-Monge et al., 1997; J. Liu et al., 2022; Maeda et al., 1993).

The idea of the extent of reaction and the best suitable samples under which conditions in terms of quality checks by either using air or nitrogen in the autoxidation process, either through blowing or bubbling and at certain higher temperatures of above 240 °C is a question of future study on the autoxidation chemistry involved in higher temperatures when nitrogen is bubbled, creates a great agitation utilizing the presence of free radicals that end up polymerizing the material and leads to very satisfactory cross-linking.

Although, it must be noted here the recommended feed out of the three tested herein is HVGO. The selection of petroleum fractions for the production of CF precursors depends on various factors such as their availability, cost, and the desired properties of the resulting precursors. However, based on existing research and the results in Table 14 (*see Appendix*

A), HVGO has been widely studied and demonstrated to be a promising feedstock for producing CF precursors due to its high aromatic content and potential for controlled autoxidation under specific conditions. Other petroleum fractions such as VGO and HT-VGO may also have potential as feedstocks for CF precursor production due to their high aromatic content, but more research is needed to fully explore their potential (Apak et al., 2002; Corscadden, 2021; Kim et al., 2021).

In addition to petroleum fractions, naphthenic-aromatic compounds can also be used as additives to improve the properties of CF precursors. Naphthenic-aromatic compounds are known to improve the oxidative stability and mechanical properties of polymeric materials, and thus, their inclusion in the precursor can lead to improved properties in the resulting carbon fiber. However, the selection of specific compounds and their optimal concentrations would require further experimentation and analysis (D. Liu et al., 2018; J. Liu et al., 2022).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In conclusion, the value addition of heavy petroleum is the future of heavy oil upgrading in the petrochemical industry. A cheap and sustainable approach was to be devised to reduce the cost of carbon fibers by utilizing cheap heavy petroleum with cheap oxidants such as air. This study examined the effects of temperature, time, and partial pressure of oxygen in autoxidizing heavy fractions of petroleum (HVGO, VGO, and HT-VGO) in a controlled semi-batch process. Key conclusions are:

- i. The autoxidation of HVGO at temperatures of 130 °C and 220 °C for 8 hours or more, and at 240–260 °C for 4 hours or more, whether by blowing or bubbling and mixing air or N_2 , unequivocally leads to a significant substantial increase in viscosity compared to raw HVGO. Remarkably, the maximum recorded viscosity reached 1979.9 cP, surpassing the viscosity of raw HVGO by approximately 1250 cP.
- ii. Bubbling air at 245 °C for 24 h resulted in a remarkable reduction of aliphatic H by 37%. Similarly, the autoxidation of another sample at 220 °C for 4 hours through bubbling air yielded comparable outcomes. Additionally, several samples subjected to heating at 240 °C for 8 h in the presence of N_2 exhibited a noteworthy improvement in aromaticity, manifested by a reduction in aliphatic H by 32%.

- iii. Notably, even at the maximum device temperature of 950 °C, the TGA normalized weight residue remained considerable at approximately 0.1 for the sample autoxidized by air for 24 h at 240 °C.
- iv. Significantly, the softening point experienced a remarkable increase under certain conditions. Noteworthy examples include the oxidation of HVGO through bubbling air at 260 °C for 8 h, as well as blowing air at 200 °C for 24 h. Furthermore, the softening point was successfully enhanced by heating HVGO in the presence of N_2 at 240 °C for 8 h, resulting in an impressive rise from 37.2 °C of raw HVGO to approximately 115 °C.
- v. Oxidized HVGO would be the most suitable carbon fiber precursor compared to the oxidized VGO and oxidized HT-VGO as viscosity change of VGO and HT-VGO were insignificant compared to the viscosity of the HVGO. It indicates the heavier petroleum fractions are better to produce carbon fiber precursor. Vacuum residues can be a potential source to produce carbon fiber precursors.
- vi. The controlled autoxidation of HVGO leads to the production of oxidized HVGO having an increase in softening point, viscosity, aromaticity, and cross-linking which are desired properties of a CF precursor. Hence, controlled autoxidation would be a potentially cheap and sustainable technique to produce CF from low-value petroleum fractions- HVGO.

It is however recommended that for the future examination and improvement of this pioneering research on the autoxidation of heavy petroleum to produce CF precursors, the following to be explored critically:

- i. Optimization studies of operating conditions for both blowing and bubbling of air or nitrogen,
- ii. Introduction/integration of chemical additives to enhance or improve the reaction products (Ucar et al., 2001),
- iii. Specify the reaction mechanism (either blowing or bubbling, with air/ N_2) with higher certainty that is more effective in the production of CF precursors.

To explore further additives, the choice of additives can have a huge impact on the properties and performance of the resulting CFs. Some commonly used additives for CF precursor production include (Coriscadden, 2021; Díez et al., 2012b; Frank et al., 2012; Park, 2015; Ucar et al., 2001):

- i. Solvents: Indene, Indan, Tetralin, Decalin, Quinoline, Pyridine
- ii. Additives: Anthracene oil, Naphthalene, Cresol, Phenol, Sulfur, Ammonia

For petroleum pitch-based CF or CF precursor, adding foreign atoms/molecules through additives can affect the final properties of the CFs. However, some solvents such as indene, indan, and tetralin that have been mentioned can act as plasticizers, softening agents, and improve the crosslinking of the pitch-based precursor material without introducing too many foreign atoms/molecules (Díez et al., 2012b; Nguyen & Lee, 2022).

Naphthenic-aromatic compounds aid in forming addition products and improving pitch properties like softening point, viscosity, and stability. By using suitable solvents and additives, pitch aromaticity can be increased, molecular weight reduced, and precursor

material's spinnability and carbonization improved (J. Liu et al., 2020; Nguyen & Lee, 2022).

The selection of additives depends on precursor material properties, composition, and desired final CF properties. Proper additives enhance mechanical and thermal properties, processability, and overall CF quality. Conversely, improper additives can lead to defects, diminished mechanical properties, and other concerns in CFs. Hence, meticulous additive selection and optimization are crucial for desired CF production outcomes (Frank et al., 2012; Park, 2015).

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2. Mohammed, L. S.; Hossain, M. M; Razzak, S. A.; Siddiquee, M. N. Prospect and Challenges of Carbon Fibre Production from Heavy Petroleum, Chemical Record (To be submitted).

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APPENDICES

Appendix-A: Viscosity Values

Table 13 Viscosity data measured at 40 °C for VGO and HT-VGO oxidized samples.

Mechanism	Gas	Experiment ID	Time, h	Temperature, °C	Viscosity, at 40 °C	B.P. in °C at 95% recovery
Bubbling and mixing	Air	A	6	130	356.3±29	550.0
		B	24	130	178.4±23	540.9
	N ₂	C	6	130	345.7±39	548.0
		D	24	130	194.0±24	547.9
	Air	E	6	130	301.9±27	539.5
		F	24	130	133.0±15	538.9
	N ₂	G	6	130	274.2±33	539.5

Table 14 HVGO data under different autoxidation conditions.

	HVGO						
Mechanism	Gas	Experiment ID	Time, h	Temperature, °C	Viscosity, at 40 °C	Softening Point, °C	B.P. in °C at 95% recovery
Blowing	Air	H	4	200	964.9±171	-	548.4
		I*	4	240	921.7±136	-	547.5
		J	4	260	827.7±155	-	539.0
		K	8	200	1173.5±150	-	542.5
		L	8	260	765.2±174	-	543.4
		M	8	240	1112.5±173	133.9	542.6
		N	24	200	1586.6±257	>200.0	546.9
	N ₂	O	4	200	809.4±155	-	548.6
		P	4	240	877.9±148	-	547.5
		Q	4	250	208.3±20	-	544.0
R		8	200	984.3±112	-	-	
S		8	240	1059.6±134	115.0	-	
Bubbling and mixing	Air	T	48	130	1979.9±99	-	-
		U	24	130	726.7±120	-	575.0
		V*	4	200	690.0±128	-	575.9
		W	4	220	660.7±108	-	545.6
		X	4	240	642.4±107	-	546.9
		Y	4	250	744.9±108	-	550.0
		Z	4	260	854.1±114	-	578.3
		AA*	8	200	917.6±250	-	578.0
		AB	8	220	878.5±116	-	548.8
		AC	8	240	1386.6±103	-	552.1
		AD*	8	260	1543.3±252	>200.0	550.8
		AE*	24	240	1919.1±220	126.6	545.3
	N ₂	AF	48	130	782.8±125	-	-
		AG	24	130	766.3±122	-	552.3
		AH	4*	240	646.0±109	-	575.9
		AI	4	220	1108.9±252	-	-
		AJ	4	200	995.1±171	-	-
		AK	8	200	1019.2±189	-	-
AL	8	240	1048.7±187	93.6	-		
- not determined, *Repeated/reproduced for reproducibility studies							

Appendix-B: TGA Data

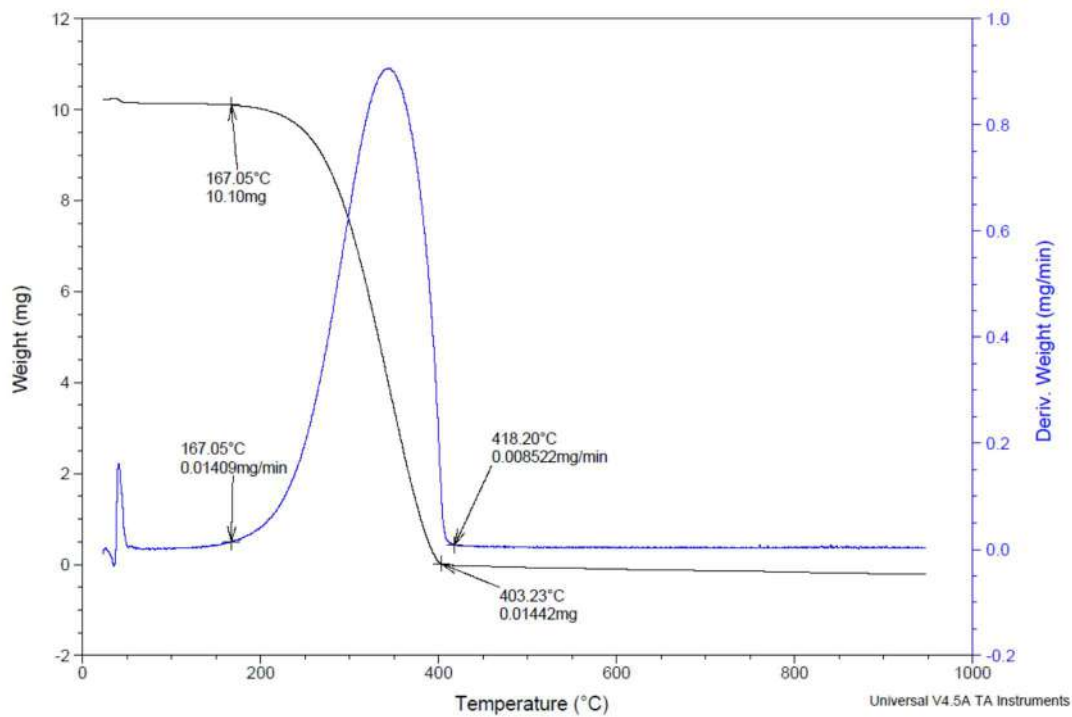


Figure 37 DSC-TGA for HVGO sample oxidized by blowing N₂ in 4 h at 240 °C.

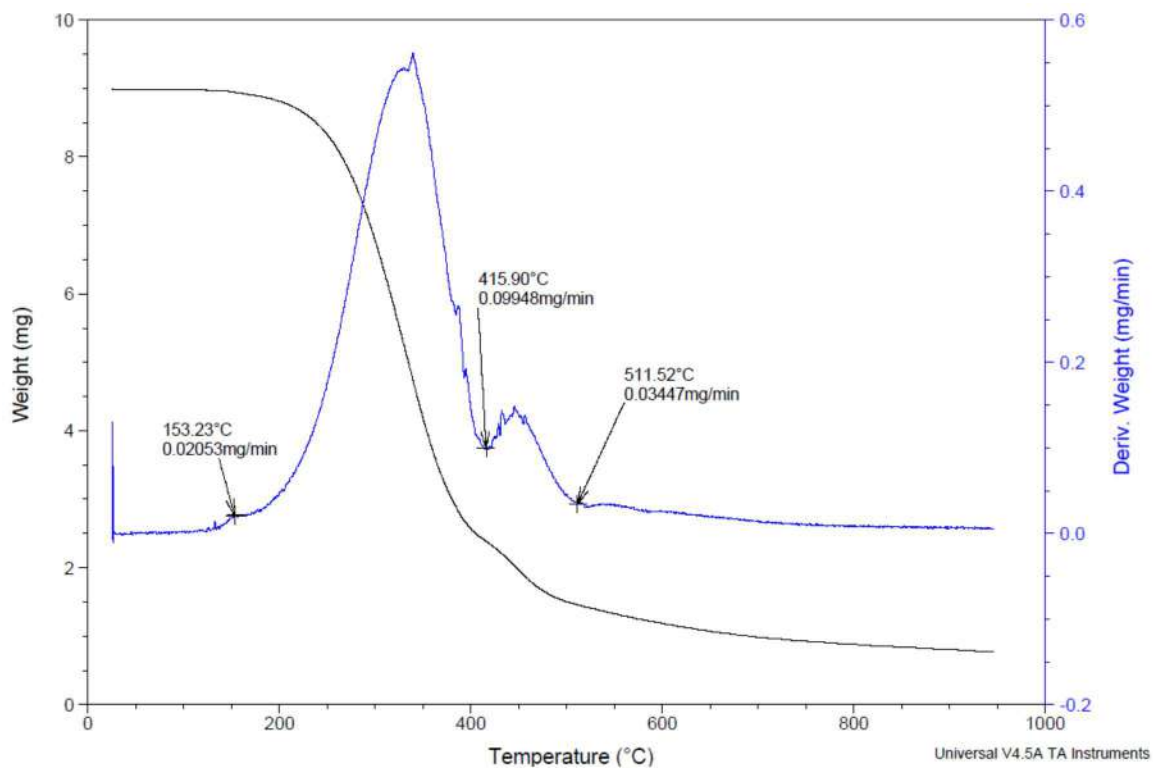


Figure 38 DSC-TGA for HVGO sample oxidized by bubbling air in 24 h at 240 °C.

Appendix-C: FT-IR Data

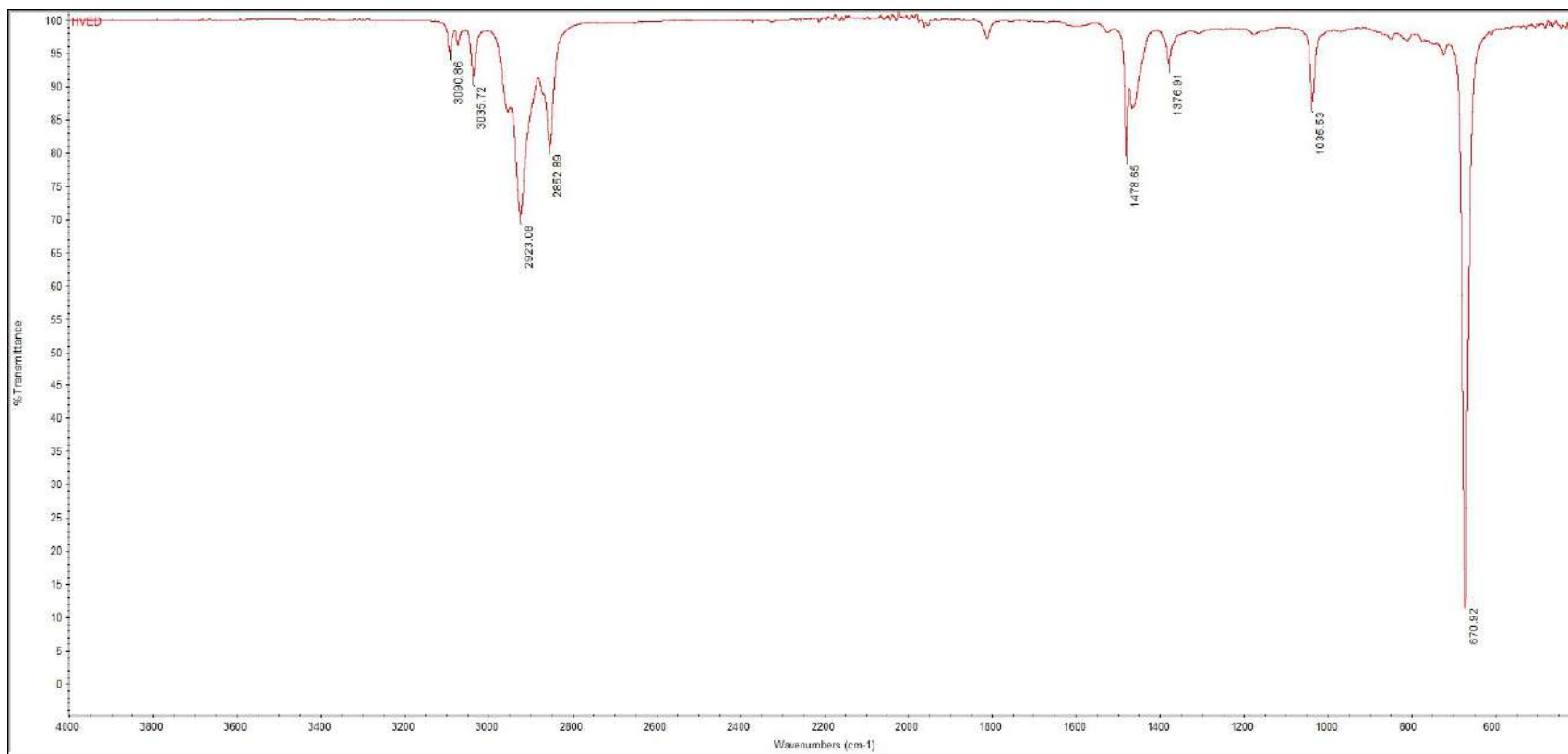


Figure 39 FT-IR spectrum for raw HVGO

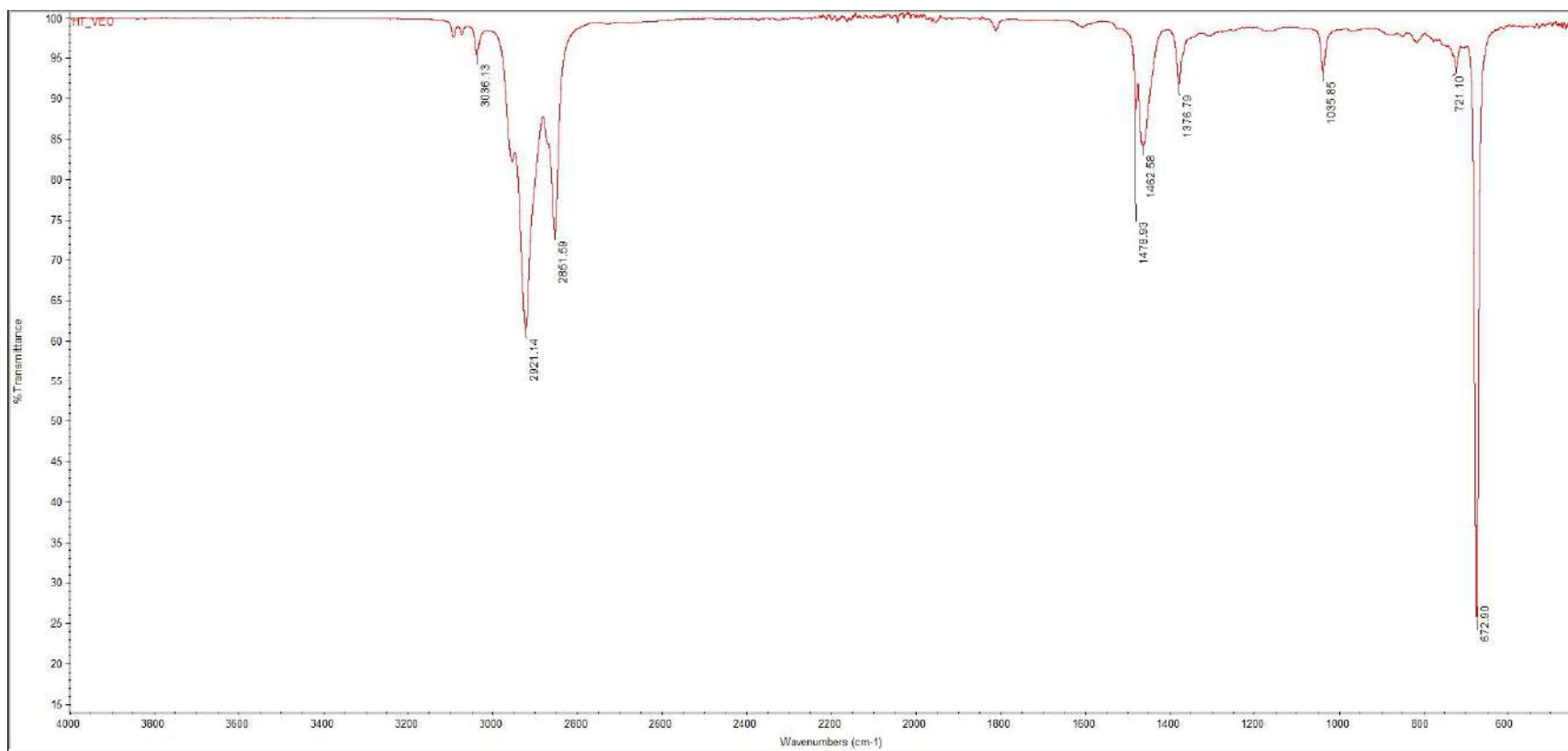


Figure 40 FT-IR spectrum for raw HT-VGO

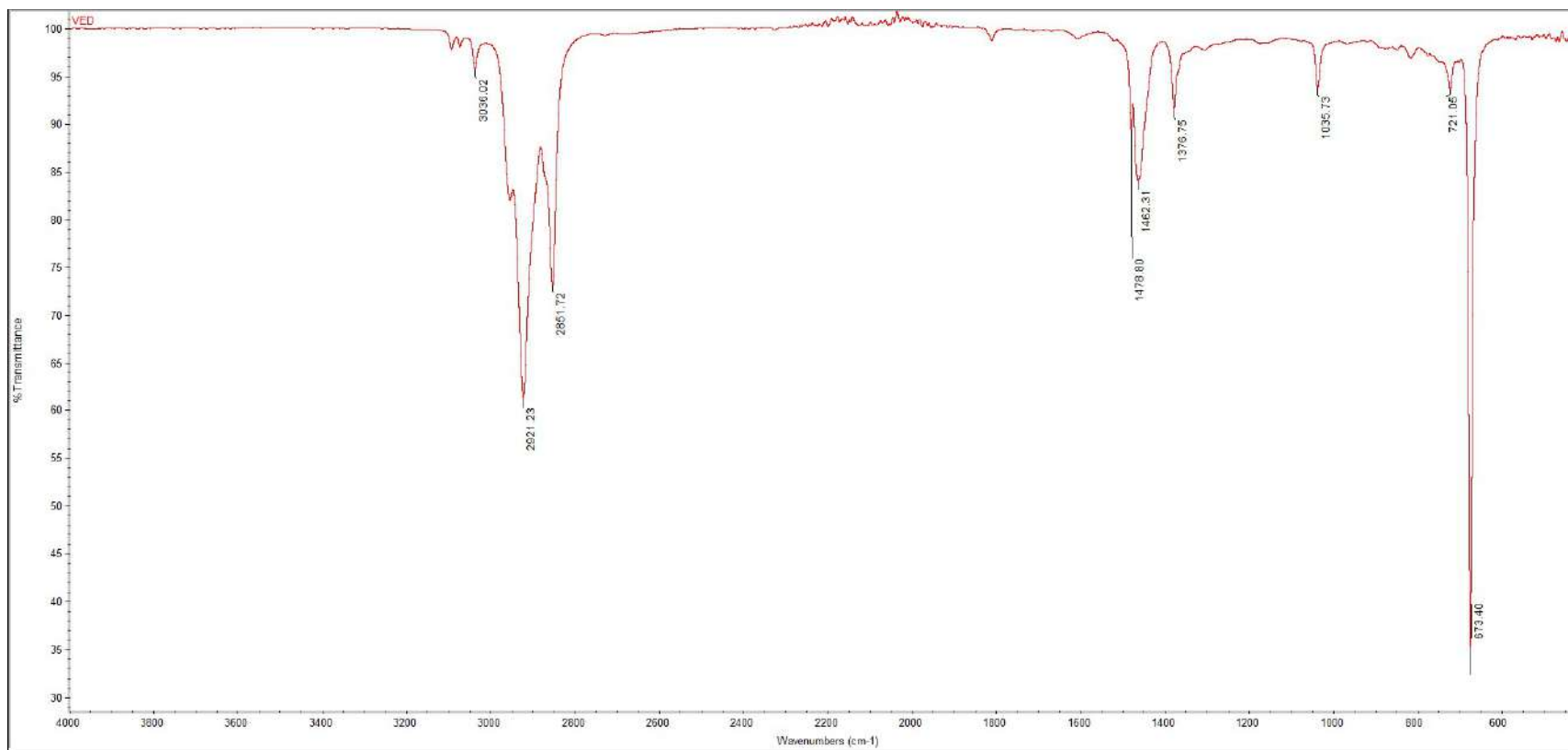


Figure 41 FT-IR spectrum for raw VGO.

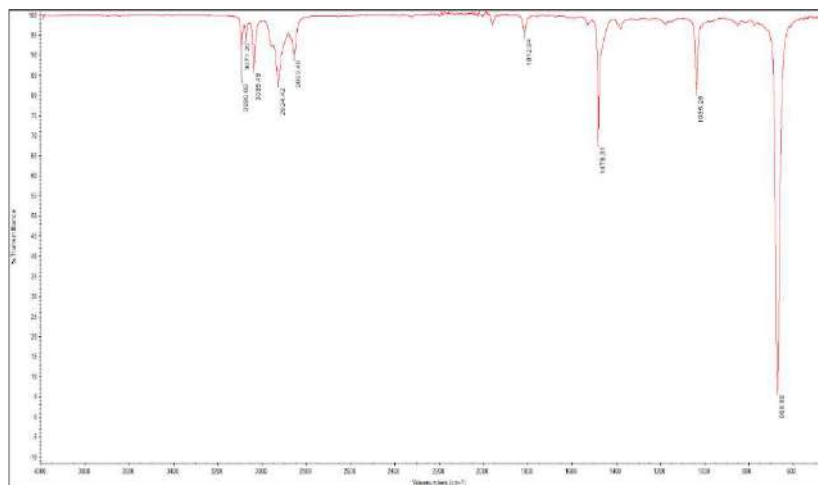


Figure 42 FT-IR spectrum for HT-VGO sample oxidized by bubbling N_2 in 24 h at 130 °C.

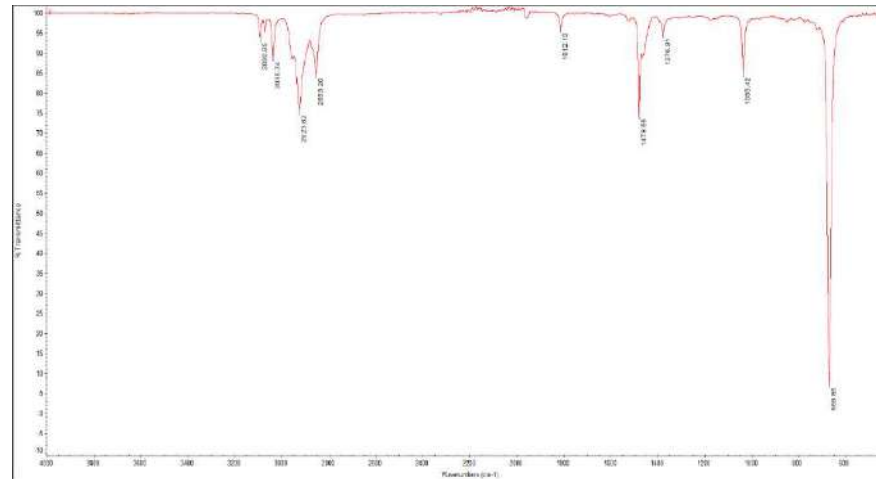


Figure 43 FT-IR spectrum for HVGO sample oxidized by bubbling air in 24 h at 130 °C.

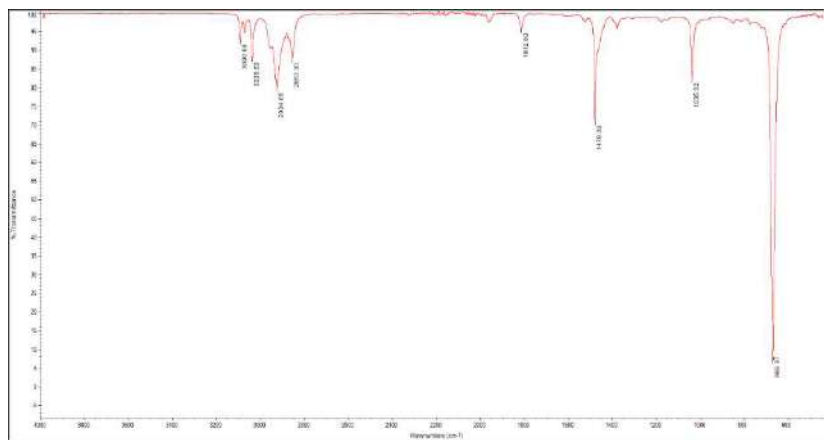


Figure 44 FT-IR spectrum for HT-VGO sample oxidized by bubbling air in 24 h at 130 °C.

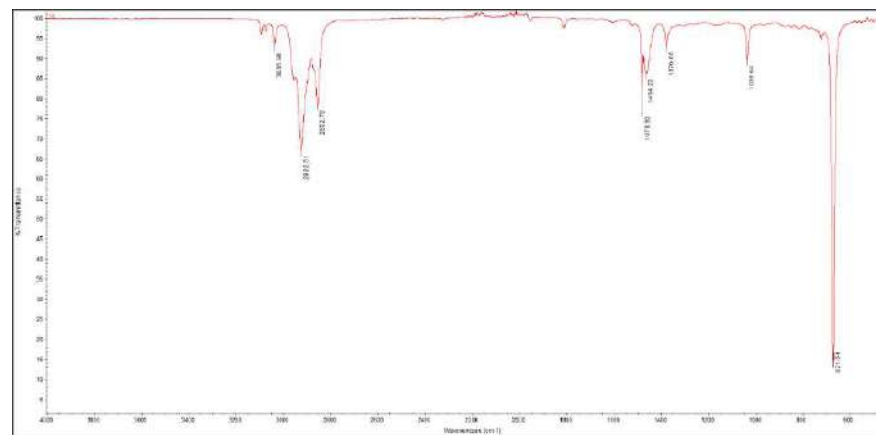


Figure 45 FT-IR spectrum for VGO sample oxidized by bubbling air in 24 h at 130 °C.

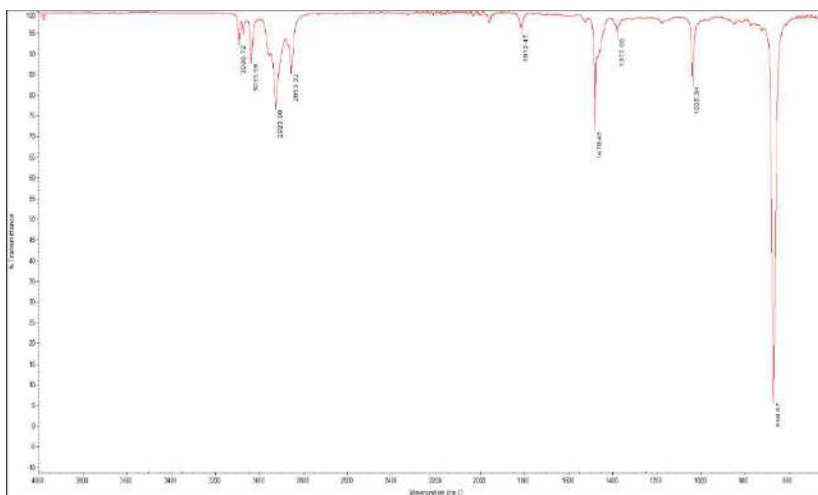


Figure 46 FT-IR spectrum for HVGO sample oxidized by bubbling air in 4 h at 200 °C.

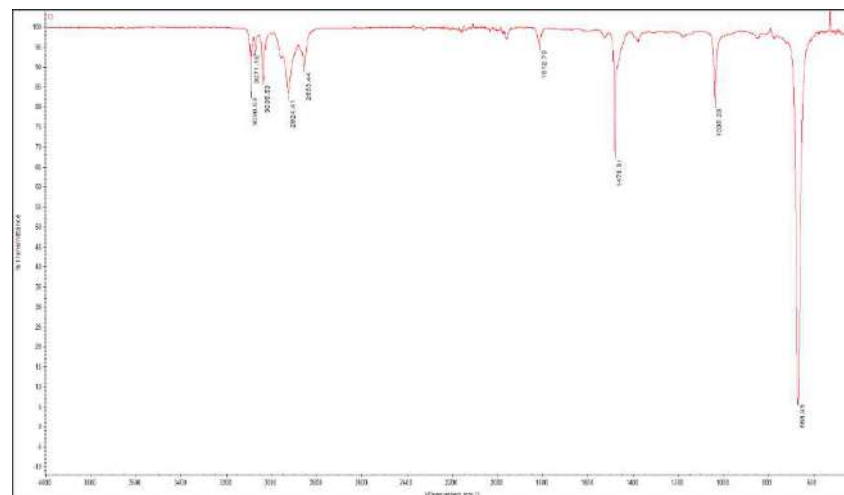


Figure 47 FT-IR spectrum for HVGO sample oxidized by bubbling air in 4 h at 220 °C.

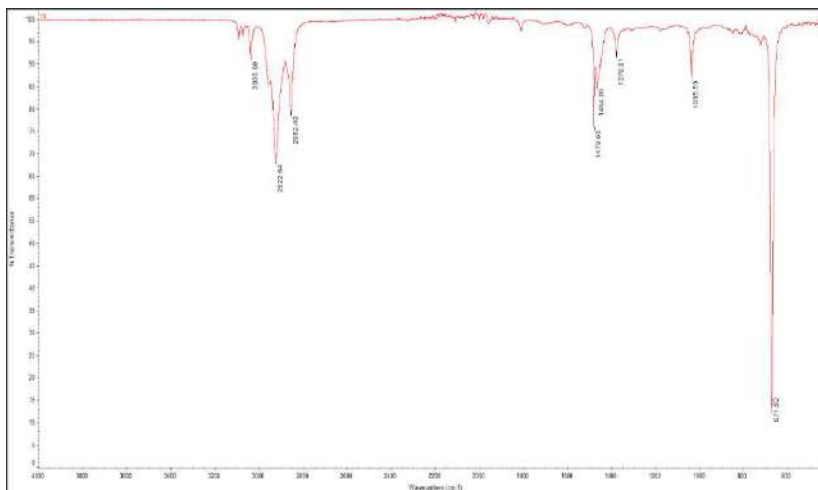


Figure 48 FT-IR spectrum for HVGO sample oxidized by bubbling air in 4 h at 240 °C.

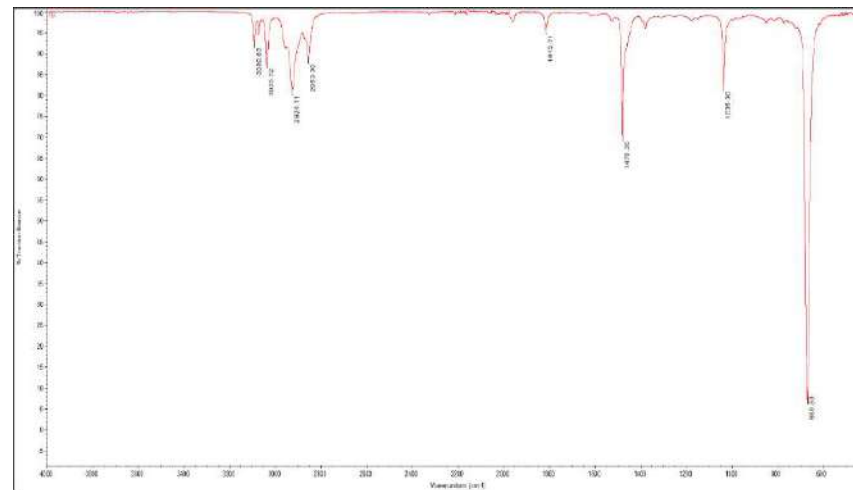


Figure 49 FT-IR spectrum for HVGO sample oxidized by bubbling N_2 in 4 h at 170–240 °C.

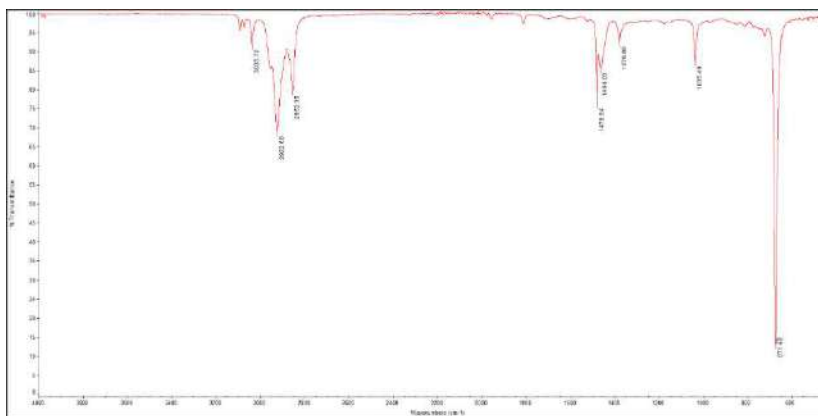


Figure 50 FT-IR spectrum for HVGO sample oxidized by bubbling air in 4 h at 250 °C.

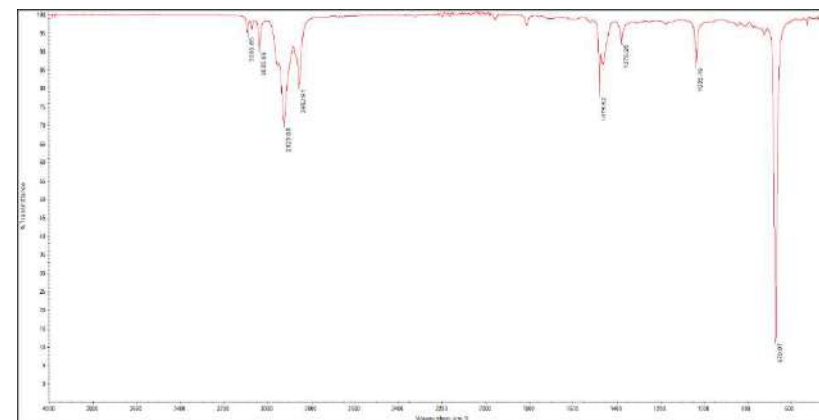


Figure 51 FT-IR spectrum for HVGO sample oxidized by bubbling air in 4 h at 240 °C.

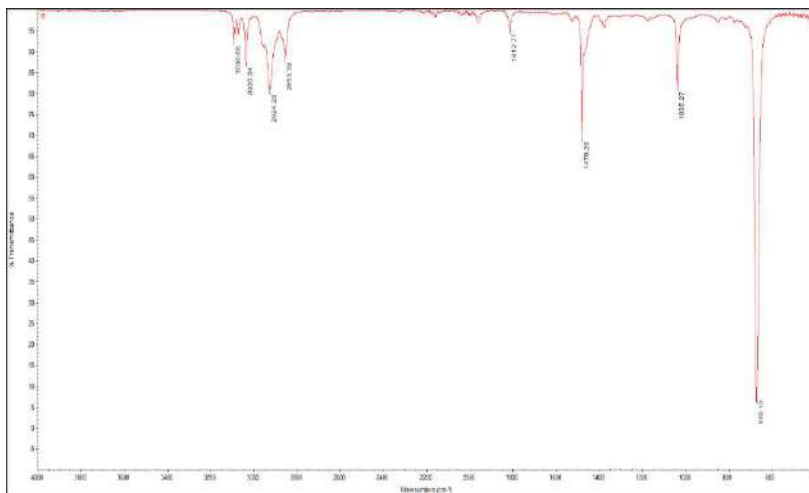


Figure 52 FT-IR spectrum for HVGO sample oxidized by bubbling air in 8 h at 200 °C.

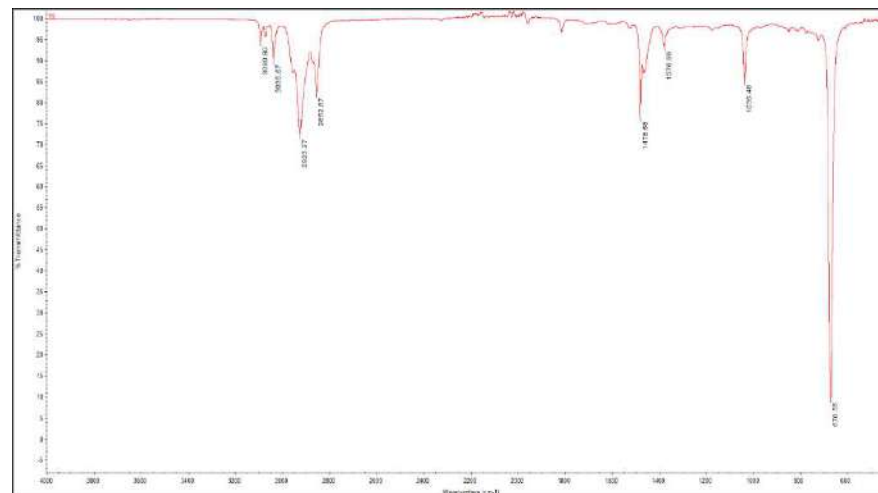


Figure 53 FT-IR spectrum for HVGO sample oxidized by bubbling air in 8 h at 220 °C.

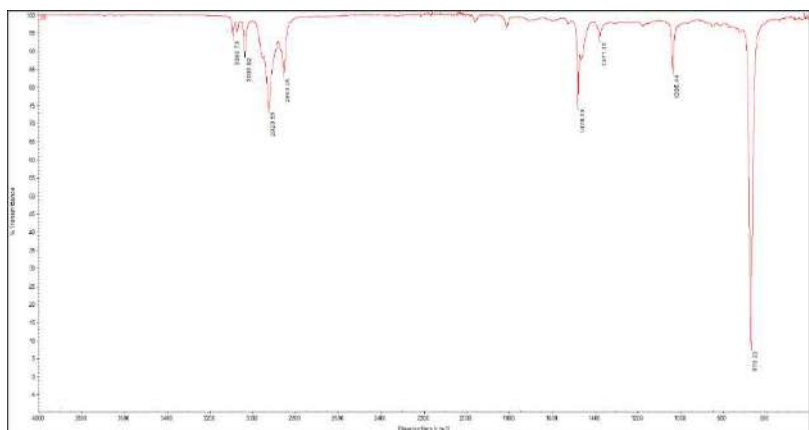


Figure 54 FT-IR spectrum for HVGO sample oxidized by bubbling air in 8 h at 240 °C.

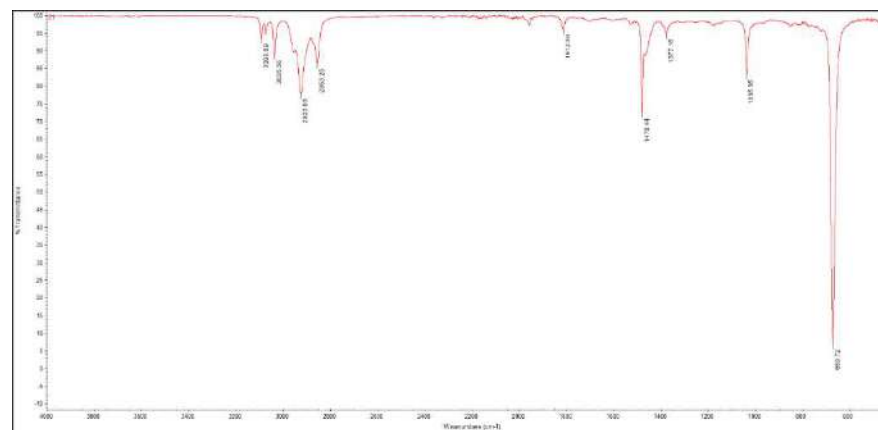


Figure 55 FT-IR spectrum for HVGO sample oxidized by bubbling air in 8 h at 260 °C.

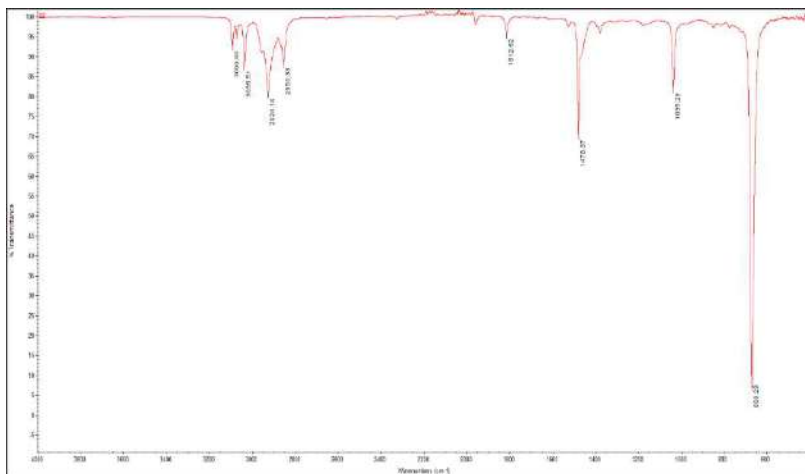


Figure 56 FT-IR spectrum for HVGO sample oxidized by blowing N_2 in 4 h at 200 °C.

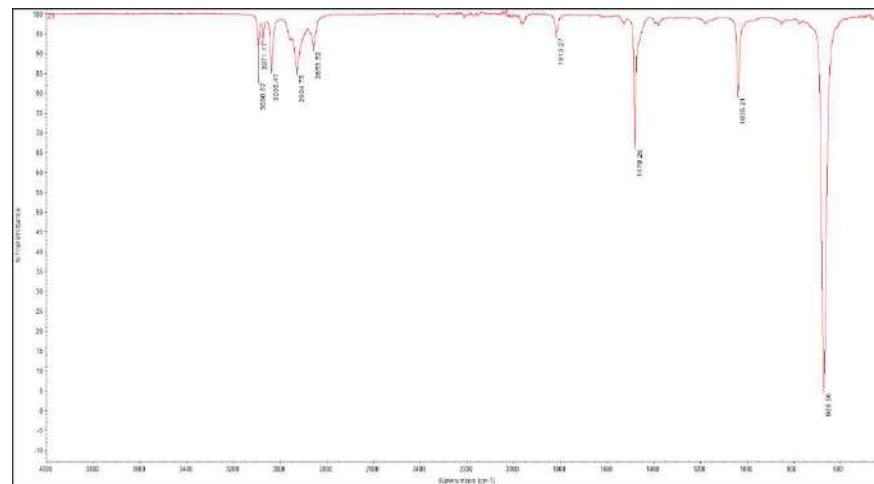


Figure 57 FT-IR spectrum for HVGO sample oxidized by blowing air in 4 h at 200 °C.

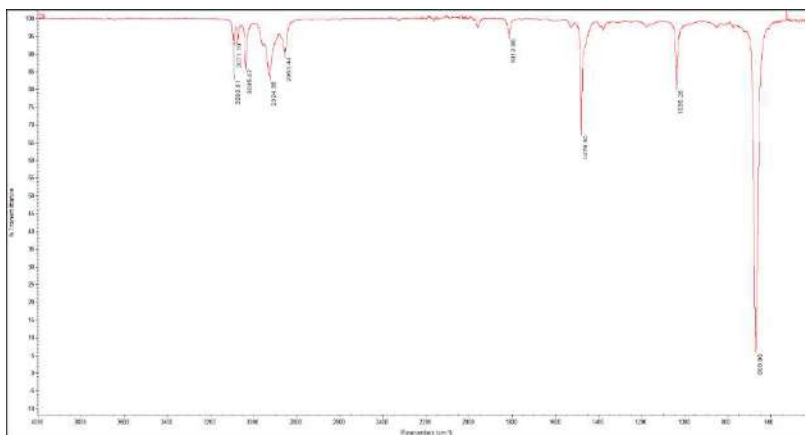


Figure 58 FT-IR spectrum for HVGO sample oxidized by blowing N_2 in 4 h at 240 °C.

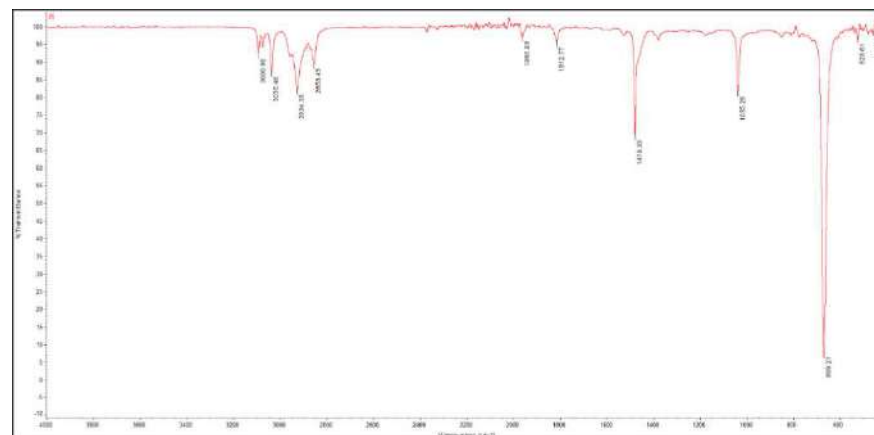


Figure 59 FT-IR spectrum for HVGO sample oxidized by blowing air in 4 h at 240 °C.

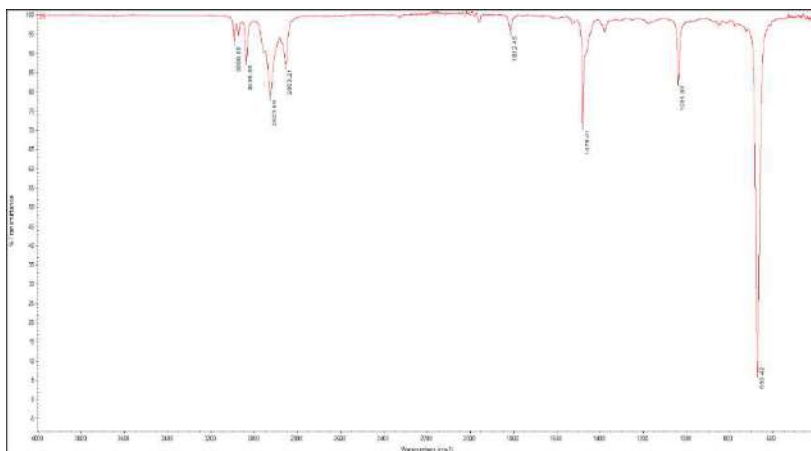


Figure 60 FT-IR spectrum for HVGO sample oxidized by blowing N_2 in 4 h at 260 °C.

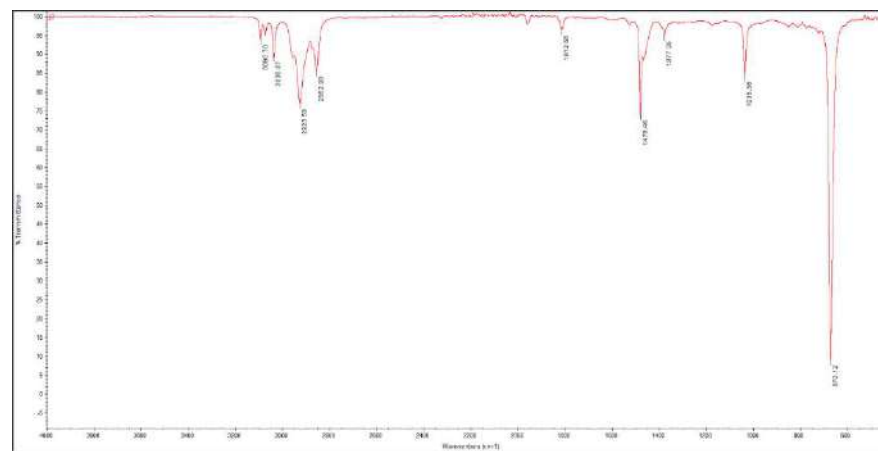


Figure 61 FT-IR spectrum for HVGO sample oxidized by blowing air in 4 h at 260 °C.

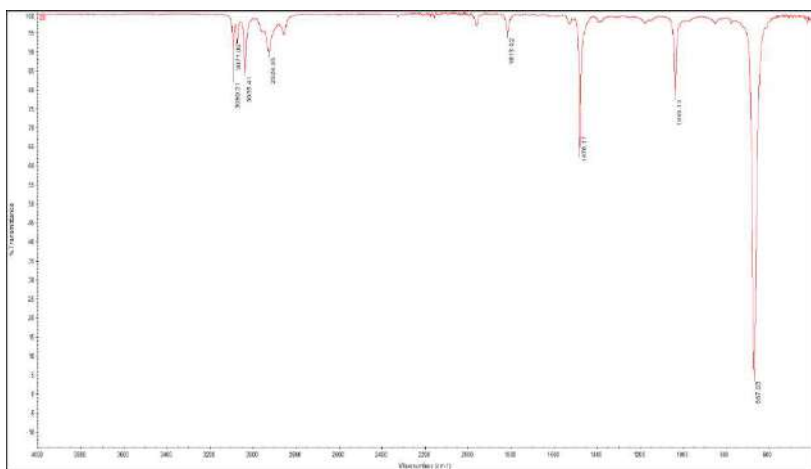


Figure 62 FT-IR spectrum for HVGO sample oxidized by blowing air in 8 h at 200 °C.

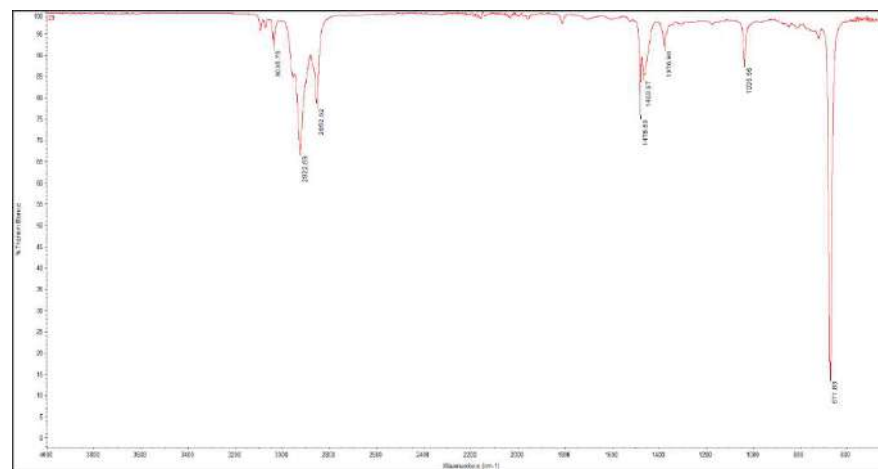


Figure 63 FT-IR spectrum for HVGO sample oxidized by blowing air in 8 h at 260 °C.

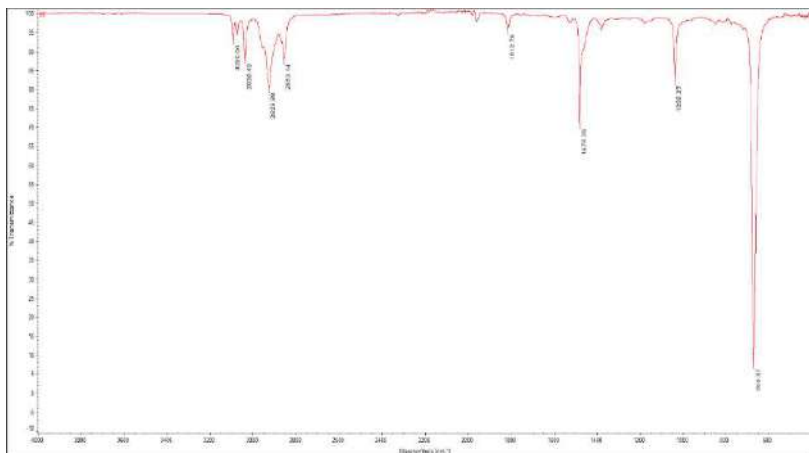


Figure 64 FT-IR spectrum for HVGO sample oxidized by blowing air in 8 h at 240 °C.

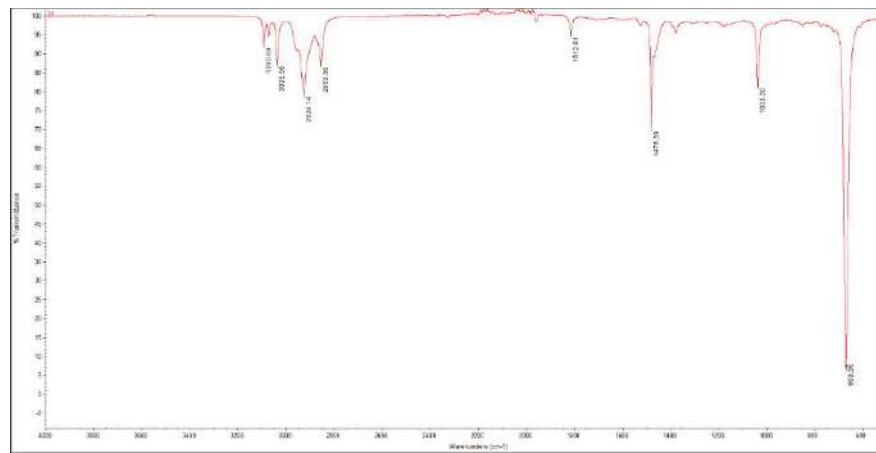


Figure 65 FT-IR spectrum for HVGO sample oxidized by blowing air in 24 h at 200 °C.

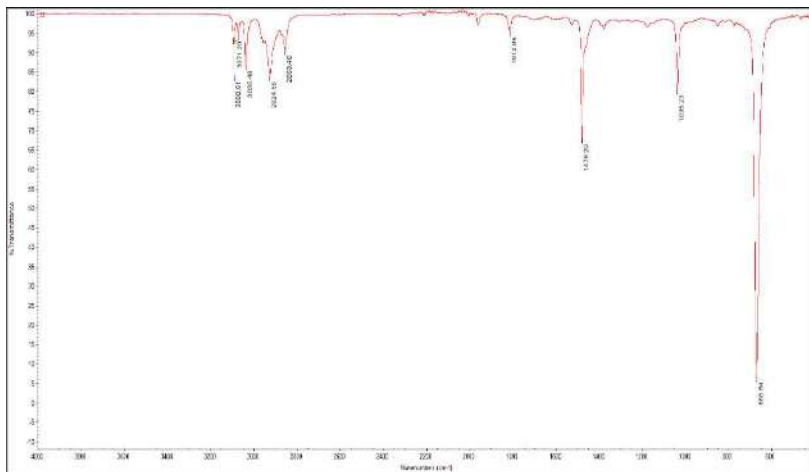


Figure 66 FT-IR spectrum for HVGO sample oxidized by bubbling air in 24 h at 240 °C.

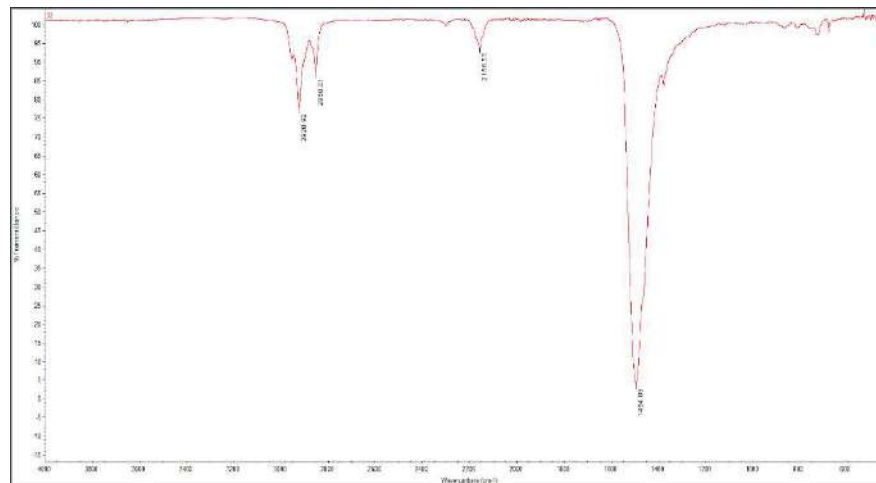


Figure 67 FT-IR spectrum for HVGO sample oxidized by bubbling N_2 in 4 h at 220 °C.

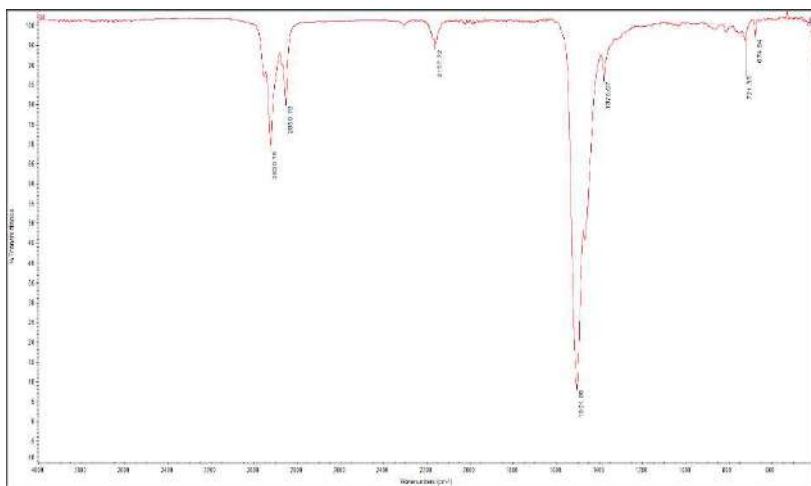


Figure 68 FT-IR spectrum for HVGO sample oxidized by bubbling N_2 in 4 h at 200 °C

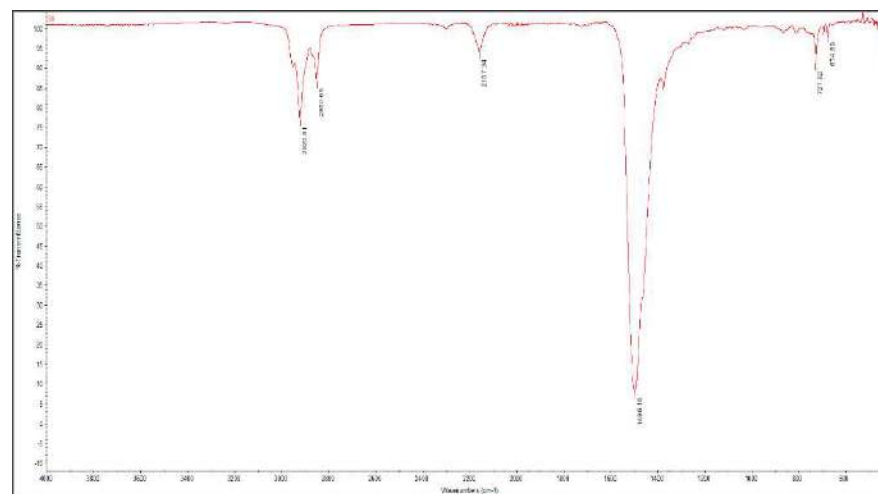


Figure 69 FT-IR spectrum for HVGO sample oxidized by bubbling N_2 in 8 h at 200 °C

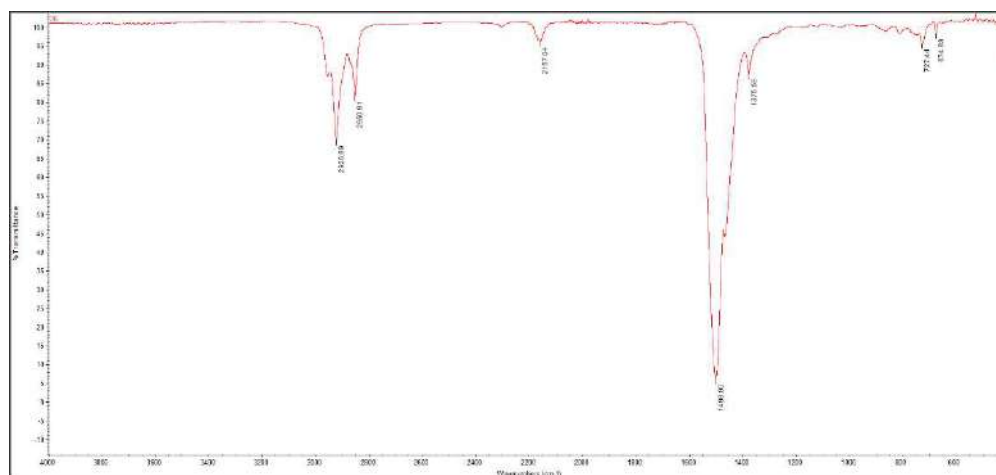


Figure 70 FT-IR spectrum for HVGO sample oxidized by bubbling N_2 in 8 h at 240 °C

Appendix-D: Photographs of the Experiments



Figure 71 Experimental Setup

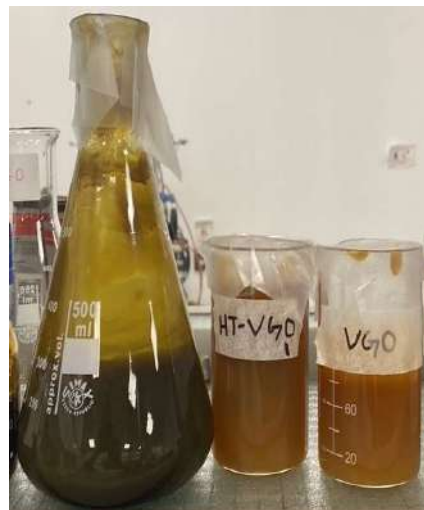


Figure 72 Photograph of raw materials



Figure 73 Photograph of proof of outbursts



Figure 74 Photograph of heavy black product deposits



Figure 75 Photograph of dissolved HVGO and product samples in CS₂



Figure 76 Photograph of manual measuring of softening point using ball-and-ring apparatus