

**PRODUCTION OF HIGH-VALUE CARBON
FIBER FROM LOW-VALUE HEAVY -
PETROLEUM FRACTIONS**

BY

Mustafa Mohammed Ali Amin

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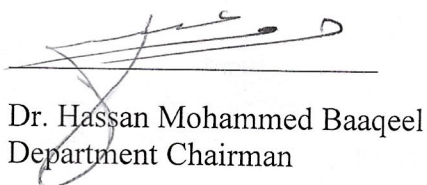
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DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Mustafa Mohammed Ali Amin** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING.**



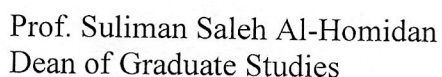
Dr. Muhammad Nurunnabi
Siddiquee
(Advisor)



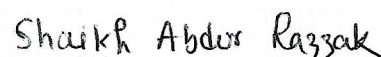
Dr. Hassan Mohammed Baaqeel
Department Chairman



Prof. Mohammad Mozahar
Hossain
(Co-Advisor)

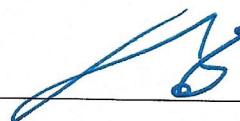


Prof. Suliman Saleh Al-Homidan
Dean of Graduate Studies



Prof. Shaikh Abdur Razzak
(Member)

Date



Prof. Mamdouh Al-Harthi
(Member)



Dr. Saad A. Al-Bogami
(External Member)

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To my beloved parents, whose love, guidance, and unwavering support have shaped every part of who I am. To my mother, whose kindness, resilience, and enduring spirit continue to inspire me in every step I take. To my father, whose wisdom, strength, and quiet encouragement have been a constant source of strength.

Though you are no longer here with me, your legacy lives on in my heart and in every achievement. This work is a testament to the values you instilled in me and is dedicated to your memory, with all my love and gratitude.

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All praise is humbly and gratefully given to Allah, the Omnipotent and the Sustainer. May His divine blessings be upon the final Prophet, Muhammad (PBUH), his family, and his close companions until the Day of Judgment. Ameen.

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LIST OF ABBREVIATIONS

CF	:	Carbon Fiber
HVGO	:	Heavy Vacuum Gas Oil
VR	:	Vacuum Residue
FT-IR	:	Fourier Transform Infrared
NMR	:	Nuclear Magnetic Resonance
TGA	:	Thermogravimetric Analysis
MS	:	Mass Spectrometry
DSC	:	Differential Scanning Calorimeter
GPCF	:	General Purpose Carbon Fibers
HPCF	:	High Performance Carbon Fibers
SIMDIST	:	Simulated Distillation
CTP	:	Coal Tar Pitch
PAN	:	Polyacrylonitrile
SEM	:	Scanning Electron Microscopy
SARA	:	Saturates, Aromatics, Resins, and Asphaltenes
SDA	:	Solvent Deasphalting
AR	:	Atmospheric residue

ABSTRACT

Full Name : Mustafa Mohammed Ali Amin
Thesis Title : Production of High-Value Carbon Fiber from Low- Value Heavy -
Petroleum Fractions
Major Field : Chemical Engineering Department
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This research evaluates the potential of low-value heavy petroleum fractions, specifically heavy vacuum gas oil (HVGO) and vacuum residue (VR), as cost-effective feedstocks for producing carbon fiber precursors. With rising demand for carbon fiber in engineering, automotive, and aviation due to its strength and lightweight properties, there is a strong incentive to explore alternatives to traditional polyacrylonitrile (PAN)-based carbon fibers, which are costly to produce. Heavy petroleum fractions offer a promising alternative due to their availability, high carbon content. However, producing carbon fiber from these fractions presents challenges that must be addressed.

The study investigates the controlled autoxidation of HVGO to enhance asphaltenes content and the physicochemical characteristics needed for carbon fiber formation. Experiments involved varying oxidation conditions, including air-blowing and bubbling techniques at different temperatures, and adding tetralin to increase molecular weight and stabilize the structure. Results showed that the autoxidation process, particularly with tetralin, significantly boosted HVGO's asphaltenes yield, achieving up to 47.2 wt%, a viscosity of 117.6 Pa.s, and a softening point of 210 °C. Melt spinning of the modified HVGO produced green fibers (70 μm diameter), which after carbonization, yielded fibers of 40-50 μm with good thermal stability as confirmed by TGA analysis.

Additionally, this study identifies the optimal conditions for transforming VR into carbon-rich asphaltenes, a suitable precursor for carbon fiber. VR oxidized at 280 °C for 10 days achieved the highest asphaltenes content (77 wt%) with a softening point of 191°C. In milder conditions, VR with 4% tetralin oxidized at 190 °C for 10 days achieved 73.2 wt% asphaltenes and a softening point of 169 °C, highlighting tetralin's impact. VR-derived asphaltenes showed excellent thermal stability, retaining 35% of their weight at 800 °C with a carbon content of 84 wt%. Green fibers spun from VR-derived asphaltenes demonstrated good spinnability, with fibers ranging from 16–25 µm in diameter and 84 wt% carbon for VR oxidized at 280 °C. These findings establish HVGO and VR as viable, cost-effective sources for carbon fiber precursors, offering a pathway to meet growing industrial demand for high-performance carbon materials.

ملخص الرسالة

الاسم الكامل: مصطفى محمد علي أمين

عنوان الرسالة: انتاج ألياف الكربون العالية القيمة من المشتقات البترولية الثقيلة المنخفضة القيمة

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: ديسمبر 2024

يقيم هذا الاستعراض الإمكانات المتاحة لاستخدام المشتقات البترولية الثقيلة منخفضة القيمة، وتحديدًا زيت الغاز ، كمصادر اقتصادية لإنتاج ألياف الكربون. ومع تزايد الطلب على (VR) وبقايا التفريغ (HVGO) الفراغي الثقيل ألياف الكربون في مجالات الهندسة والسيارات والطيران نظرًا لقوتها ووزنها الخفيف، هناك دافع قوي لاستكشاف التي تعتبر مكلفة في الإنتاج. تمثل (PAN) بدائل لألياف الكربون التقليدية المصنوعة من مادة البولي أكريلونيتريل الكسور البترولية الثقيلة بديلاً واعدًا نظرًا لتوافرها وارتفاع محتواها الكربوني وإمكانية استخدامها كموارد مستدامة. ومع ذلك، تواجه عملية إنتاج ألياف الكربون من هذه الكسور تحديات يجب التغلب عليها.

بهدف زيادة محتوى الأسفلتين وتحسين الخصائص HVGO تتناول الدراسة عملية الأكسدة الذاتية المضبوطة للـ الفيزيائية والكيميائية المطلوبة لتشكيل ألياف الكربون. وشملت التجارب تعديل ظروف الأكسدة، بما في ذلك تقنيات ضخ الهواء والبلق عند درجات حرارة مختلفة، مع إضافة التترالين لزيادة الوزن الجزيئي واستقرار التركيب. أظهرت ، حيث HVGO النتائج أن عملية الأكسدة الذاتية، خاصة مع إضافة التترالين، زادت بشكل كبير من نسبة الأسفلتين في وصلت إلى 47.2% من الوزن، مع لزوجة بلغت 117.6 باسكال ثانية، ونقطة تليين عند 210 درجة مئوية. وأنتجت المعدل ألياف خضراء بقطر 70 ميكرومتر، والتي أنتجت بعد الكربنة أليافًا بقطر HVGO عملية الغزل الذائب لـ TGA يتراوح بين 40-50 ميكرومتر وذات استقرار حراري جيد كما أكد تحليل.

إلى أسفلتين غني بالكربون يصلح ليكون مادة أولية VR بالإضافة إلى ذلك، تحدد هذه الدراسة الظروف المثلى لتحويل لألياف الكربون. حيث بلغت نسبة الأسفلتين 77% من الوزن ونقطة تليين وصلت إلى 191 درجة مئوية عند أكسدة مع 4% من التترالين المؤكسد VR عند درجة حرارة 280 مئوية لمدة 10 أيام. وفي ظروف أكثر اعتدالاً، حقق VR عند 190 درجة مئوية لمدة 10 أيام نسبة أسفلتين بلغت 73.2% من الوزن ونقطة تليين عند 169 درجة مئوية، مما

استقرارًا حراريًا ممتازًا، حيث احتفظت بنسبة 35% VR يبرز تأثير التترالين. وأظهرت الأسفلتينات المستخرجة من من وزنها عند 800 درجة مئوية وبلغ محتواها الكربوني 84%. كما أظهرت الألياف الخضراء المغزولة من سهولة في الغزل بقطر يتراوح بين 16–25 ميكرومتر ونسبة كربون 84% بالنسبة VR الأسفلتينات المستخرجة من كمصادر اقتصادية VR و HVGO المؤكسد عند 280 درجة مئوية. تؤكد هذه النتائج على إمكانية استخدام VR للفعالة لإنتاج ألياف الكربون، مما يوفر مسارًا مستدامًا لتلبية الطلب الصناعي المتزايد على المواد الكربونية عالية الأداء.

CHAPTER 1 |

INTRODUCTION

1.1 Background

Carbon fiber is highly valued for its exceptional mechanical properties, such as high tensile strength, low weight, and remarkable thermal and chemical stability, making it a sought-after material in industries like aerospace, automotive, renewable energy, and sporting goods. The global demand for carbon fiber has seen rapid growth, rising from 25,000 metric tons in 2009 to 120,500 metric tons in 2022, with projections reaching 143,500 metric tons by 2025, as illustrated in **Figure 1**. Industry revenue is anticipated to grow at an annual rate of 10.9% from 2023 to 2030, driven by the expanding use of carbon fiber composites, particularly in wind turbine blades for renewable energy. **Figure 2** presents an overview of the carbon fiber production process, which involves several stages: precursor pretreatment, spinning, oxidative stabilization, carbonization, and potentially graphitization. This process produces two main types of carbon fiber: high-performance (HP) and general-purpose (GP). HP carbon fiber, used in high-demand sectors like aerospace and automotive, as illustrated in **Figure 2**, provides enhanced properties, while GP carbon fiber is suited to less rigorous applications, such as sporting goods and automotive parts (Schade *et al.*, 2017)(Park et al., 2001)

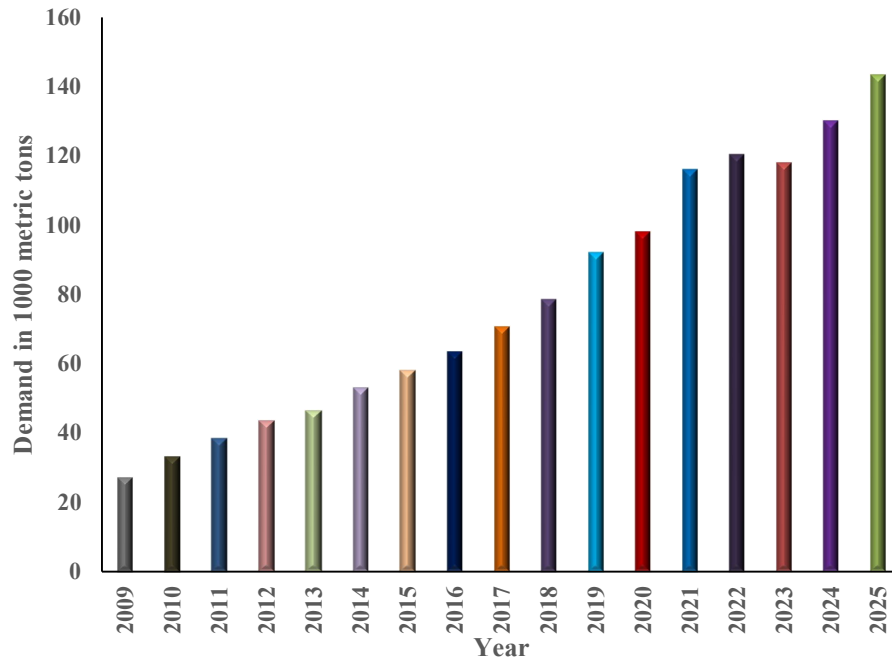


Figure 1. World demand for carbon fiber in 1,000 metric tons from 2009 to 2022 (Amin et al., 2024).

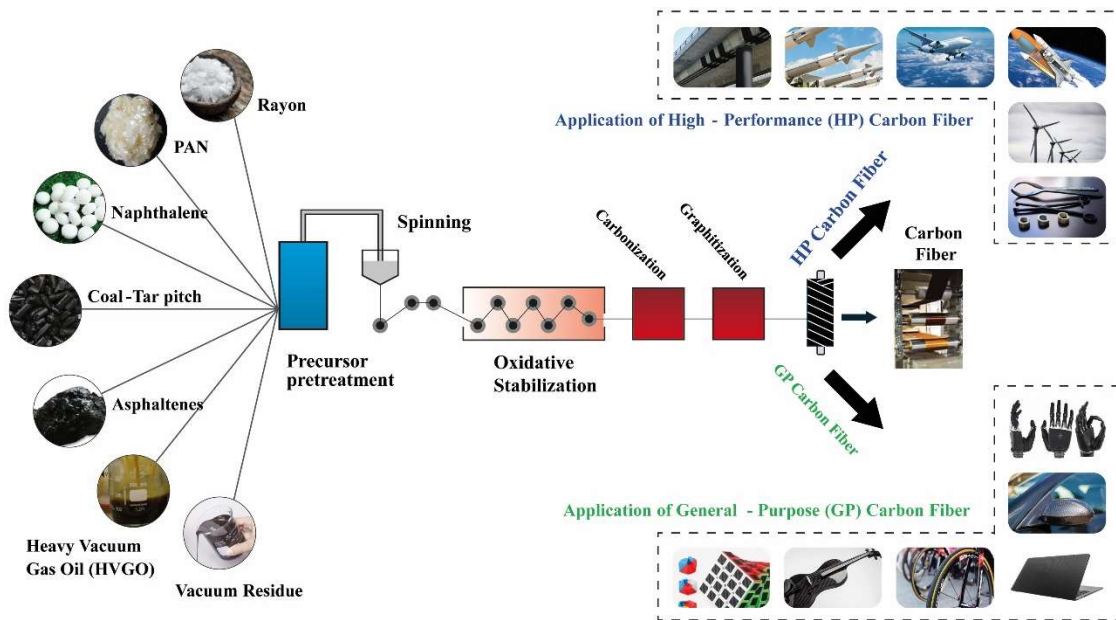


Figure 2. Overview and application of carbon fiber (Amin et al., 2024).

However, producing carbon fiber is expensive, largely due to the high cost of traditional precursors like polyacrylonitrile (PAN) and the energy-intensive nature of the production process. With increasing demand, finding alternative, cost-effective precursor materials is essential. Heavy petroleum fractions, such as vacuum residue (VR) and heavy vacuum gas oil (HVGO), offer a promising alternative as carbon fiber precursors. These fractions are rich in carbon, structurally aromatic, and have the potential to significantly reduce production costs while making use of resources that are often underutilized (Bajpai, 2021).

As shown in **Figure 3**, the petroleum industry generates a broad range of products through crude oil refining, separating lighter fractions, like gases, at the top of the distillation column and leaving heavy fractions, such as VR and HVGO, at the bottom. These heavy fractions, with their high molecular weight and complex structures, are generally seen as low-value by-products due to their high viscosity and storage challenges. The industry typically focuses on producing lighter, more marketable fractions, while heavy fractions are channeled toward low-efficiency uses, like combustion and asphalt production, or processed further through costly upgrading methods, such as coking and hydrocracking (Yadav et al., 2023).

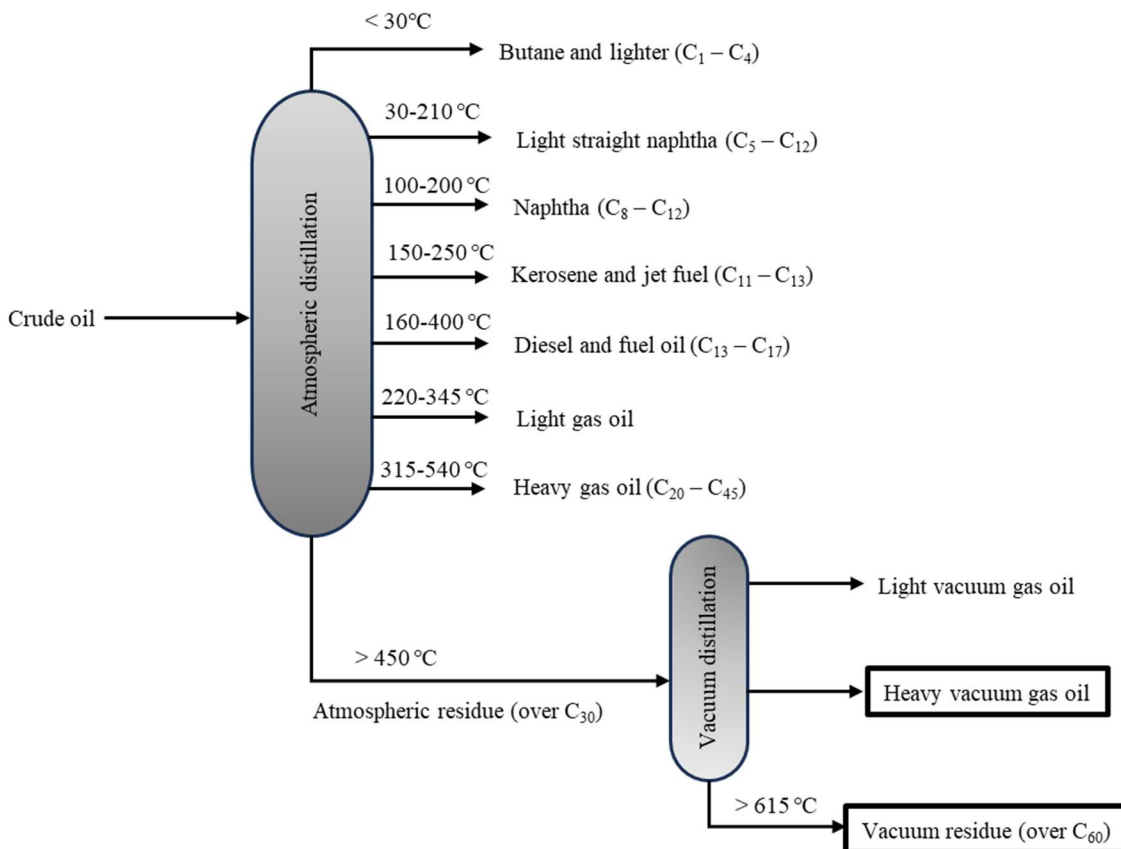


Figure 3. Typical fractional distillation of crude oil (Siddiquee, 2024).

As illustrated in **Figure 4**, [a] and [b], different types of crude oil contribute distinctively to the production of petroleum fractions. The pie chart in **Figure 4** [a] shows the proportions of various crude types: conventional oil (30%), oil sands bitumen (30%), extra heavy oil (25%), and heavy oil (15%). This distribution highlights the prevalence of heavier oils, like oil sands bitumen and extra heavy oil, which yield larger amounts of high-molecular-weight components that are challenging to refine. The abundance of these heavier oils contributes to the significant availability of heavy fractions, aligning with industry concerns about their underutilization. **Figure 4** [b] further explores the composition of these oil types by depicting the boiling point fractions for each category of crude oil across various global sources. The bar chart indicates the relative volume of high-

boiling (above 524°C) and low-boiling (below 524°C) fractions for oil sands bitumen from Canada, Gulf of Mexico crude, Upper Zakum medium crude from the UAE, Ebok heavy crude from Nigeria, and Kazakhstan light crude. Notably, heavier oils like Canadian oil sands bitumen and Ebok heavy crude exhibit a greater proportion of high-boiling fractions, shown in black. These high-boiling fractions, characterized by their density and resistance to flow, demand energy-intensive refining processes or are often relegated to low-value uses (Mao et al., 2022).

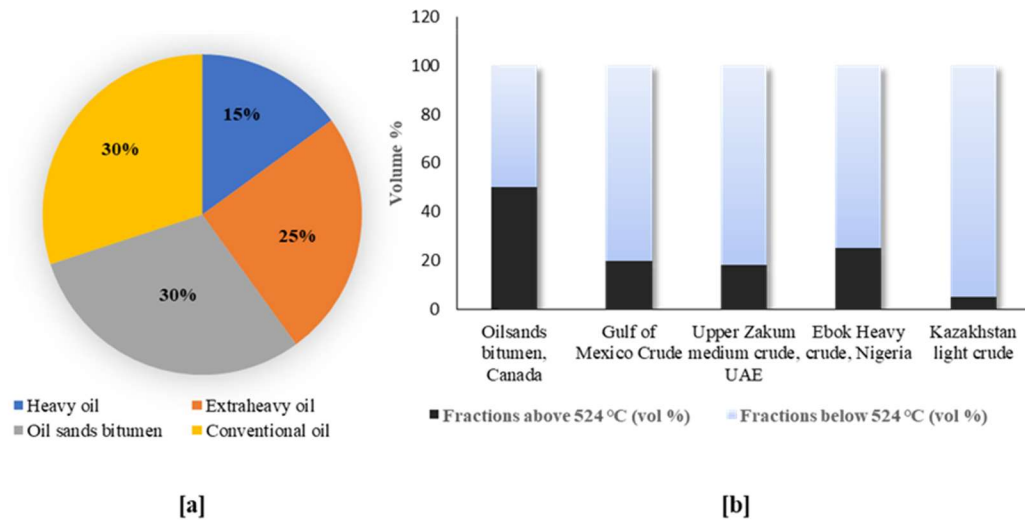


Figure 4. Total world oil reserve (Siddiquee, 2016).

With global crude oil refining at such a large scale, a substantial amount of heavy petroleum fractions is produced. As demand for lighter fuels increases, refineries generate even more heavy residues. These fractions are typically channeled toward low-efficiency uses like combustion, asphalt production, or undergo energy-intensive processes such as coking and hydrocracking to produce lighter hydrocarbons. However, these uses do not fully capitalize on the inherent value of heavy fractions (Siddiquee, 2016).

Using heavy petroleum fractions as alternative precursors for carbon fiber presents a two-fold advantage: it adds significant value to an underused resource and has the potential to reduce carbon fiber production costs. Given their high carbon content and aromatic structure, these heavy fractions are promising candidates for carbon fiber production after suitable processing. This approach aligns with sustainable goals by promoting efficient resource use and reducing waste (Carreón-Calderón et al., 2021).

One of the main research challenges in producing carbon fiber from heavy petroleum fractions lies in enhancing the mechanical strength of petroleum-derived carbon fibers for diverse applications. Strengthening carbon fibers derived from petroleum is not straightforward. In addition to improving pretreatment processes for carbon fiber precursors, it is important to develop composite lattice designs and fabrication techniques to impart the necessary properties for various applications. For instance, innovative designs such as 3D-weaved carbon fiber lattices have shown promise. Considering the potential applications for petroleum-based carbon fiber in areas like hydrogen storage, pipelines, construction, and batteries, further research into appropriate lattice designs, fabrication techniques, and performance evaluation processes is essential. Moreover, efficient, sustainable recycling processes for high-strength carbon fiber could expand its use across diverse fields (Amin et al., 2024).

An additional research gap is the lack of a holistic approach to environmental and sustainability considerations in carbon fiber production from heavy petroleum fractions. While some studies address these aspects, a comprehensive life cycle analysis and environmental impact assessment are often missing. Addressing this gap is essential for

developing sustainable practices, ensuring that the use of heavy petroleum fractions positively impacts the industry's ecological footprint (McClintock et al., 2023).

Finally, the economic feasibility of large-scale carbon fiber production from heavy petroleum fractions warrants further study. Comprehensive economic analyses, covering production costs, scalability, and competitiveness with traditional carbon fiber precursors, are often absent in current research. Addressing these economic gaps will provide essential insights into the feasibility and potential challenges of adopting this approach on an industrial scale (Ellringmann et al., 2016).

1.2 Research Objectives

The primary aim of this study was to develop a sustainable, cost-effective, and efficient pre-treatment method for transforming heavy petroleum fractions into carbon fiber precursors via controlled autoxidation (air oxidation), ultimately producing carbon fiber from these precursors. The specific objectives were as follows:

- i. To examine the thermal effects on carbon fiber precursor production from heavy petroleum fractions, utilizing different air addition techniques including blowing air without mixing and air bubbling with mixing.
- ii. To assess the role of naphthenic aromatic hydrocarbons, particularly tetralin, under conditions similar to those in the first objective.
- iii. To evaluate the suitability of the produced precursors from objectives 1 and 2 as carbon fiber precursors by testing their spinnability using a melt-spinning machine and carrying out subsequent steps to produce carbon fiber.

1.3 Research Novelty

This research introduces a novel approach to synthesizing asphaltenes directly from heavy vacuum gas oil (HVGO), which initially contained no asphaltenes, by increasing their asphaltenes concentration through tetralin addition. Unlike conventional methods, this study successfully generated asphaltenes within HVGO through a controlled autoxidation process, followed by direct extraction of the newly formed asphaltenes. These asphaltenes were subsequently processed to create green fibers, showcasing HVGO's potential as a precursor for carbon fiber production. Additionally, in contrast to prior studies, this work achieved green fiber production from vacuum residue (VR) directly following a single pre-treatment step, bypassing the solvent extraction stage typically required for asphaltenes separation. This innovative method presents a promising new pathway for converting low-value petroleum fractions into high-value materials.

1.4 Scope and Outline of the Work

This scope provides a comprehensive approach to assessing heavy petroleum fractions as alternative carbon fiber precursors through systematic autoxidation and characterization processes and to achieve the goals are as follows:

Investigation of Thermal and Time Effects in Autoxidation Pre-treatment: This study explores the impact of temperature and reaction time on autoxidation as a pre-treatment for carbon fiber precursors, utilizing two types of heavy petroleum feedstocks: heavy vacuum gas oil (HVGO) and vacuum residue (VR). Experimental conditions include:

- Temperature range: 160°C to 280°C
- Oxidation time: 1 to 10 days
- Air addition methods: air bubbling with mixing and air blowing without mixing.

Role of Naphthenic Aromatic Hydrocarbons in Autoxidation: Under the same temperature, time, and air addition conditions, this study examines the effect of naphthenic aromatic hydrocarbons, particularly tetralin, on autoxidation. Tetralin concentration is varied from 0 to 30 wt.% to assess its impact on enhancing the oxidation process and on the formation of carbon-rich structures.

Evaluation of Heavy Petroleum Fractions as Carbon Fiber Precursors: The potential of the pre-treated heavy petroleum fractions as carbon fiber precursors is evaluated based on their physical and chemical properties. Key parameters examined include boiling point ranges, aromaticity, molecular weight, viscosity, thermal stability, and H/C ratios (aliphatic

and aromaticity indices). Spinnability testing is conducted using a melt-spinning machine, followed by additional steps to produce carbon fiber, with selective analysis and discussion of these properties presented in the study.

The structure of this thesis is organized as follows:

- **Chapter 1** provides a comprehensive overview of heavy petroleum fractions, their properties, availability, and potential as precursors for high-value materials.
- **Chapter 2** briefly elaborated a literature review on the general topic of controlled autoxidation of heavy oils to produce carbon fiber precursors.
- **Chapter 3** details the experimental methodologies, including the processing techniques adapted for heavy fractions and the characterization methods used.
- **Chapter 4** presents the results of the experiments, analyzing the properties and performance of the carbon fibers produced from Heavy Vacuum Gas Oil (HVGO).
- **Chapter 5** presents the results of the experiments, analyzing the properties and performance of the carbon fibers produced from Vacuum Residue (VR).
- **Chapter 6** concludes the study with a summary of key insights, considerations of limitations, and recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

The primary objective of this study was to develop a sustainable, cost-effective, and efficient pre-treatment method for converting heavy petroleum fractions into carbon fiber precursors through controlled autoxidation (air oxidation), ultimately producing carbon fiber from these precursors. To support this goal, it is essential to have a foundational understanding of carbon fiber (Section 2.1), including its types (Section 2.2) and production methods (Section 2.3), as well as the pitch preparation methods which include the autoxidation method and its chemistry involved (Section 2.4) and the role of naphthenic aromatic hydrocarbons (Section 2.5). A comprehensive review of relevant literature focused on experimental methods and result interpretation is presented in the respective chapters (Chapters 3 and 4). This chapter, however, serves as the initial groundwork, offering a starting point for the investigation.

2.1 Carbon Fiber: Overview

Carbon fibers have been in existence since 1879. Thomas Edison subjected cotton threads or bamboo silvers to high temperatures, causing them to undergo carbonization and transform into a filament made entirely of carbon fiber. These carbon fibers have various advantages over other types of fibers, such as superior chemical resistance, light weight, high mechanical strength, high stiffness, very low thermal expansion, and versatility (Perumal et al., 2020). Due to these properties, carbon fiber is commonly recognized as

one of the high-performance materials and has found application in defense, aerospace, automobile, civil engineering, motorsports, and military, along with other allied fields. While carbon fibers offer superior properties and performance, especially when mixed with other carbon materials to form carbon-carbon composites, their cost remains comparatively high against similar fibers like those made of glass or plastic (Gonçalves et al., 2023).

Figure 5 provides a depiction of a typical carbon fiber along with its scanning electron microscopy (SEM) image and a typical chemical structure. The production process involves transforming precursor materials like polyacrylonitrile (PAN), pitch, or rayon through spinning, oxidative stabilization, carbonization, and optional graphitization. PAN-based carbon fibers are favored for their superior mechanical properties, while pitch-based fibers offer cost advantages. Ongoing advancements in production methods, including the exploration of alternative precursors and sustainable practices, contribute to the continual evolution of carbon fiber technology, ensuring its sustained relevance and growth in various applications. With a diameter ranging from 5 to 10 micrometers, carbon fiber's ultra-light yet exceptionally strong nature has led to its increased utilization across industries, with properties influenced by both the production process and the raw materials employed.

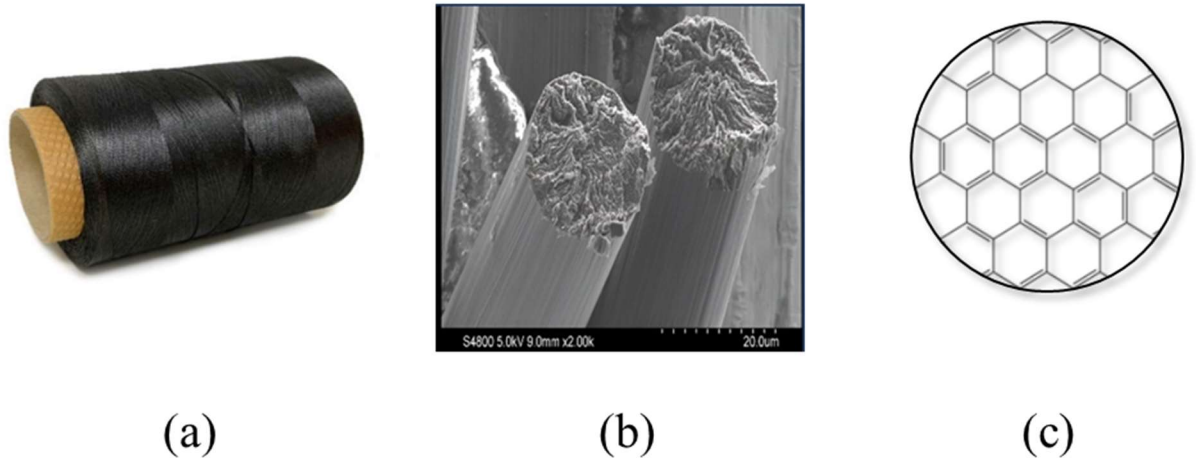


Figure 5: (a) Typical roll of carbon fiber filaments, showcasing the woven material; (b) Microscopic image of carbon fiber filaments with visible fracture surfaces (c) hexagonal lattice structure of single-layer carbon fiber (Melanson, 2023).

2.2 Types of Carbon Fiber

Carbon fibers are categorized based on their precursors, performance, and commercial availability. Based on the precursor type, carbon fiber can be PAN-based, pitch-based, biomass-based carbon fibers, or synthetic polymers such as phenolic and polybenzimidazole (**Figure 6**). Key subtypes within each category are further delineated, offering a concise representation of the diverse materials used in carbon fiber production. Carbon fiber production encompasses a multifaceted process traditionally dominated by two primary sources: PAN-based and pitch-based methods. Polyacrylonitrile serves as the most common precursor, undergoing complex processes like oxidation and carbonization to yield carbon fibers known for their high tensile strength and modulus, suitable for aerospace, automotive, and sports equipment applications (Huang, 2009). Pitch-based carbon fibers, derived from petroleum or coal tar byproducts, offer cost advantages despite

challenges in achieving the desired strength, including mesophase formation and stabilization (Aldosari et al., 2020). Rayon-based carbon fibers, although less commonly used, exhibit unique characteristics such as good electrical conductivity, with a production process involving carbonization and graphitization (Moulefera et al., 2021). **Figure 7** illustrates the typical chemical structures of different precursors. **Figure 7 (a)** depicts the mostly used typical PAN precursor, derived from the polymerization of acrylonitrile, often facilitated by a catalyst in a reaction medium. **Figure 7 (b)** displays a cellulose unit, which

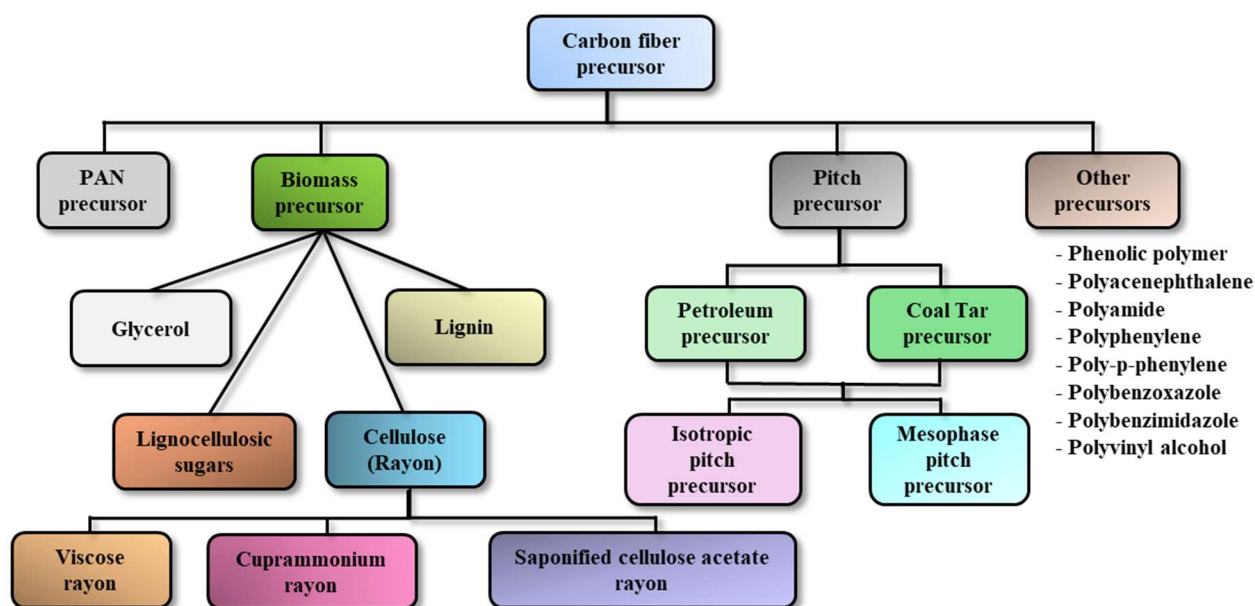
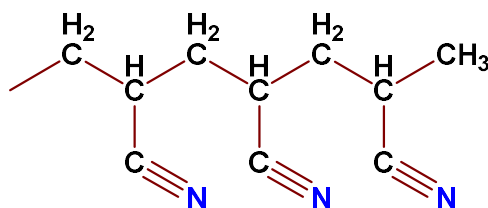


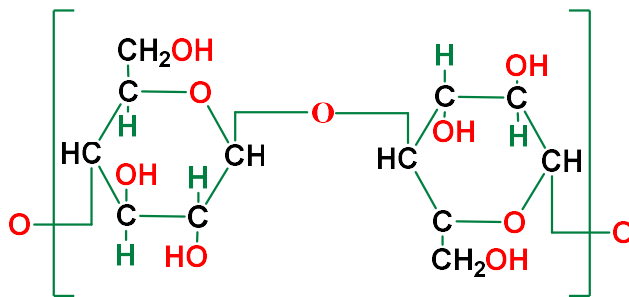
Figure 6. Types of carbon fiber precursors.

serves as the starting material for rayon carbon fiber production. The process of producing cellulose units involves multiple steps, including the extraction, purification, and conversion of cellulose into a form suitable for spinning (Kaur et al., 2016).

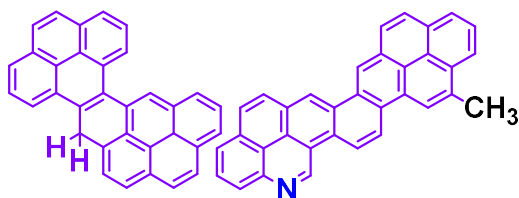
(a) Polyacronitrile (PAN)



(b) Cellulose unit



(c) Coal-Tar pitch precursor



(d) Petroleum pitch precursor

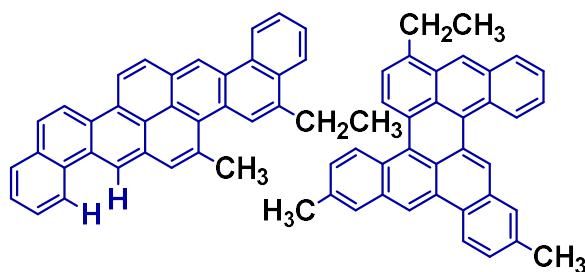


Figure 7. The image displays four typical precursors used in the production of carbon fiber: (a) polyacrylonitrile (PAN); (b) cellulose; (c) a coal tar pitch; and (d) a petroleum pitch precursor.

Additionally, the elevated production costs and variable quality make them less preferable compared to alternative precursors like PAN. Pitch precursors, portrayed in **Figures 7 (c) and 7 (d)**, primarily sourced from coal or crude oil, pose unique challenges owing to their complex composition of numerous molecules. Coal tar pitch precursors often have a higher concentration of aromatic compounds and yield more carbon compared to petroleum pitch precursors. However, they often necessitate more rigorous purification methods to reduce impurities and maintain consistent quality during carbon fiber manufacturing (Kershaw & Black, 1993).

Based on their performance according to their tensile moduli (**Table 1**), carbon fibers are categorized into ultrahigh-modulus (UHM), high-modulus (HM), intermediate-modulus (IM), high tensile strength (HT), and isotropic carbon fibers (IC). UHM shows a tensile modulus > 500 GPa, while HM shows a tensile strength > 300 GPa. The choice of fiber type depends on performance and cost, ensuring the best balance between performance and cost (Ko et al., 2020)

Table 1. Reported mechanical properties of various carbon fiber classes (J. Liu et al., 2020).

Fiber type	Acronym	Tensile strength [GPa]	Young's modulus [GPa]	Maximum elongation (%)
Ultra-high modulus	UHM	~ 3	≥ 500	$\sim 0.5\%$
High modulus	HM	2–4.5	350–450	$\geq 1\%$
Intermediate modulus	IM	4–7	250–350	$> 1\%$
High tension	HT	3–5	200–250	1.5–2%
Isotropic	IC	0.5–1.0	30–50	$\geq 1.5\%$

PAN-based carbon fibers have an intermediate modulus over 200 GPa, while high-modulus fibers can reach up to 600 GPa (**Figure 8**). Pitch-based precursors for carbon fiber production, derived from petroleum and coal tar, have sub-optimal tensile strength, limiting their use in advanced structural applications (**Figure 8**). Rayon as a precursor for carbon fiber production presents economic challenges due to low yields and the requirement for fiber stretching at high temperatures, leading to increased production costs (Sefiu Adekunle Bello, 2021).

Exploration into alternative polymers as precursors for carbon fibers has incorporated various other natural fibers like silk, chitosan, and eucalyptus, providing a potential reduction in production costs. **Figure 7** illustrates a schematic categorization of these precursor materials. Nonetheless, these predominantly yield general-purpose carbon fibers, which are compromised in mechanical strength. Researchers have thoroughly investigated the viability of a number of linear and cyclic polymers as precursors, including phenolic polymers, polyaceneophthalene, polyamide, polyphenylene, poly-p-phenylene benzobisthiazole (PBBT), polybenzoxazole, polybenzimidazole, polyvinyl alcohol, polyvinylidene chloride, and polystyrene. In order to fabricate high-performance carbon fibers, linear precursors usually result in much lower carbon outputs (Kossakowski & Dygas, 2023).

Additionally, carbon fibers can be categorized as General-Purpose (GP), High-Performance (HP), or Activated Carbon Fibers (ACF) based on their availability in the commercial sector. The GP-carbon fibers, due to their amorphous and isotropic structures, are characterized by a lower tensile strength and modulus but are economically advantageous owing to their reduced cost. Conversely, HP-carbon fibers exhibit elevated strength and modulus, standing in stark contrast to their GP counterparts. One characteristic that sets HP-carbon fibers apart is the correlation between a greater modulus and both stronger anisotropy and a higher proportion of graphite in the fiber structure. This distinction emphasizes the inherent variances in structural and mechanical properties, correlating with the diversity in commercial applications and pricing structures between the differing types of carbon fibers (Perepelkin, 2002).

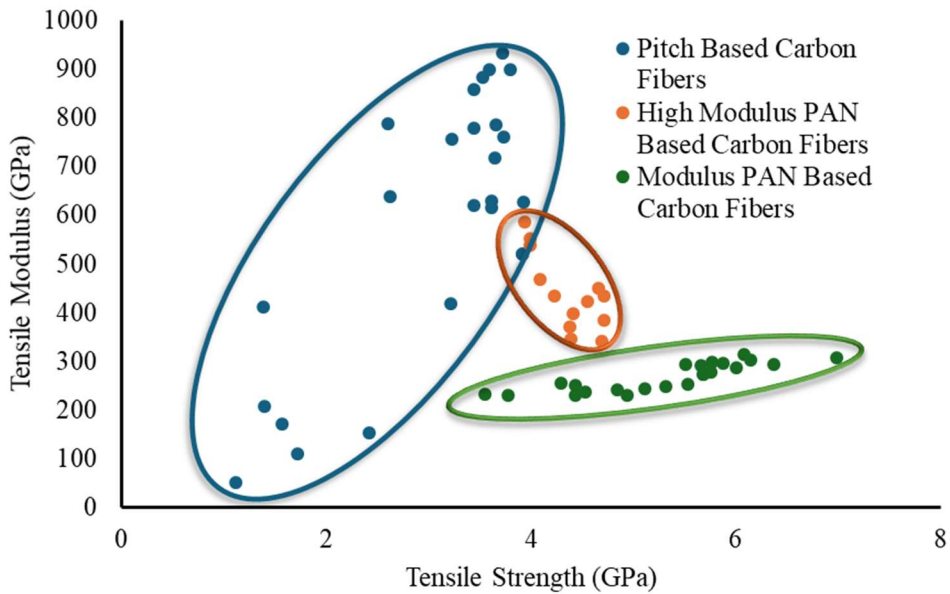


Figure 8. Tensile Modulus and Strength of High and Intermediate Modulus Pitch- and PAN-Based Carbon Fibers (Newcomb, 2016).

In summary, the overview underscores the significance of PAN and pitch-based methods, while ongoing research endeavors strive to explore novel precursors and processing techniques, meeting the escalating demand for carbon fibers with improved cost efficiency and sustainability. The categorization of carbon fibers is complex, involving several factors such as tensile strength, modulus, precursor materials, and commercial accessibility. Therefore, it is crucial to carefully choose the appropriate carbon fiber type that matches the specific needs of various industrial applications and considers economic factors (Newcomb, 2016).

2.3 Carbon Fiber Production

Carbon fiber production is a complex and specialized process. This section provides a quick overview of the production of carbon fiber, a multi-step process that includes precursor preparation, spinning, oxidative stabilization, carbonization, and graphitization (**Figure 10**). The production of carbon fiber begins with the crucial step of preparing precursors, a process contingent on the type of raw materials chosen, as illustrated in **Figure 7**. The following sections thoroughly explore the intricate nature of pitch precursors, illuminating the complexities involved in their utilization for carbon fiber production. This detailed examination is essential for understanding the specific challenges and considerations associated with pitch-based carbon fibers.

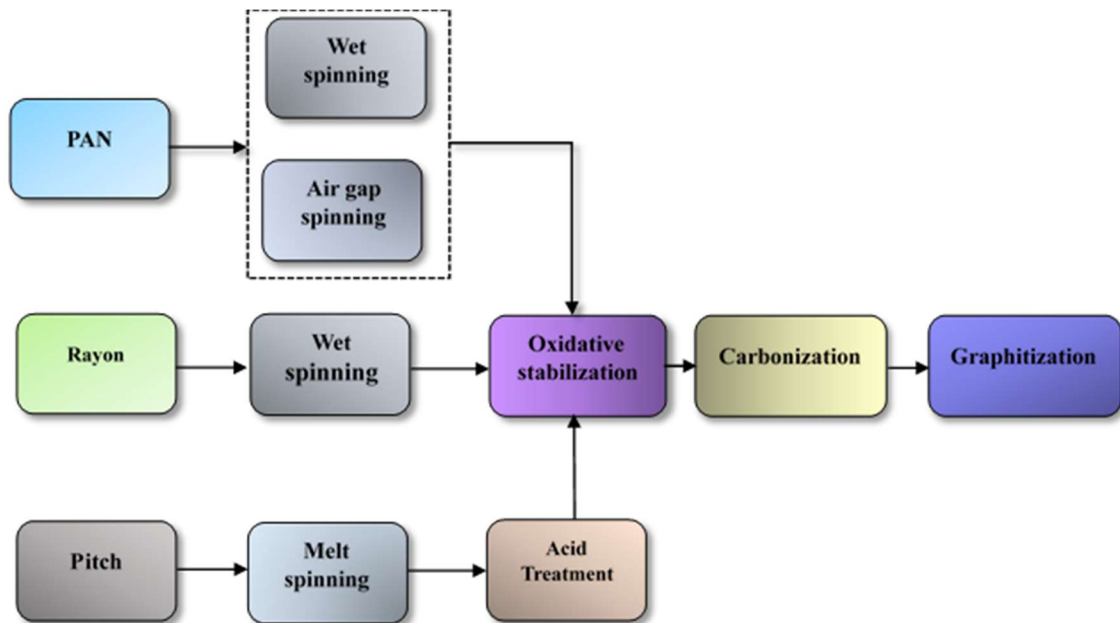


Figure 9. Steps for carbon fiber production from various precursors.

The spinning of carbon fiber precursors involves converting raw materials like polyacrylonitrile (PAN), rayon, or pitch into continuous filaments, each using a tailored spinning mechanism. Traditionally, PAN-based carbon fibers are produced through wet spinning, where the polymer solution is extruded into a coagulation bath, but this method is increasingly being replaced by dry-jet wet spinning (air gap spinning). This technique introduces an air gap between the spinneret and the bath, enhancing polymer chain alignment and improving the fibers' mechanical properties. Rayon, derived from regenerated cellulose, follows a similar wet spinning process. Pitch, from petroleum or coal tar sources, is processed through melt spinning, where initially the precursor is heated until it reaches a highly viscous state and is then forcibly extruded through a spinneret to form filaments. These filaments are subsequently cooled and hardened. During this process, the filaments are pulled to align the polymer chains, enhancing their tensile qualities, and are then wound around spools. Every spinning technique, including wet spinning, air gap spinning, and melt spinning, is specifically developed to enhance the molecular alignment and physical characteristics of carbon fibers. This guarantees that the fibers satisfy the strict demands of their intended uses and uphold the utmost standards of quality and performance (Alice Landmér, 2022).

Following the spinning process, the oxidative stabilization step is crucial for transforming the spun fibers into a form suitable for carbonization. During this phase, the fibers are heated in the air at temperatures ranging from 200 to 300 °C. This controlled oxidation process promotes the cross-linking of the polymer chains within the fibers, which stabilizes their structure and prevents melting during the subsequent high-temperature carbonization stage (Maheshwari, 2019).

The subsequent carbonization process in carbon fiber production involves heating the stabilized fibers to temperatures ranging from 1000 °C to 1500 °C in an inert atmosphere. This controlled environment causes the vaporization of non-carbon elements and facilitates the formation of densely packed carbon layers that resemble graphene sheets. This transformative step not only significantly increases the carbon content of the fibers, often surpassing 90% by weight, but also plays a pivotal role in defining their final mechanical, thermal, and electrical properties (L. Liu et al., 2023).

In certain cases, the production process may include an additional step called graphitization, where the fibers are subjected to even higher temperatures, typically exceeding 2000 °C. This extra step further refines the organization and alignment of the carbon layers within the fibers, as illustrated in **Figure 5**. The outcome is an enhancement in the mechanical, thermal, and electrical properties of the fibers. This meticulous control and refinement at each stage of carbon fiber production are essential to ensuring that the final product adheres to the desired specifications, making it suitable for diverse applications in fields such as aerospace, automotive, sports equipment, and construction (Guo et al., 2016). The ability to tailor the properties of carbon fibers through precise control of the carbonization and graphitization processes is key to their widespread and successful application in various industries.

Producing carbon fibers from alternative synthetic polymers necessitates tailored precursor preparation and specific thermal processing. The choice of polymer dictates the spinning method and influences the stabilization and carbonization conditions to achieve the desired carbon fiber characteristics, accommodating the unique requirements of each polymer for optimal performance (Edwards et al., 2003). Transforming carbon fiber precursors into a

graphene-like structure, as shown in **Figure 5**, presents considerable challenges, including the need for high-temperature processing in an inert atmosphere, precise alignment of precursor molecules, achieving uniform graphitization, and preserving tensile strength. Additionally, the energy-intensive nature of the graphitization process and the potential for reduced carbon yield contribute to increased production costs and complexity.

2.4 Pitch Precursors and Their Preparation

Poly aromatic hydrocarbons (PAHs) that demonstrate a wide range of molecular weights, spanning from 200 to 1600 Da. This range of pitches exhibits the ability to be customized for various carbon products with distinct molecular weight distributions. Consequently, it can be utilized as a promising source material for the manufacturing of carbon fibers or as carbon fillers in composite materials. The pitches can have a composition that includes a carbon content above 80%. The specific composition of the pitches can vary depending on the source tar and the processing parameters used (Berrueco et al., 2012).

This section discusses the methodologies employed in the preparation of these pitches, and preparing the groundwork for a deeper understanding of their role in carbon fiber production.

2.4.1 Preparation of Isotropic Pitch Precursors

In-depth discussion of isotropic precursor preparation is provided, looking into petroleum pitch and the processes used to create carbon fiber precursors from it. General-purpose (GP) pitch carbon fibers are a type of carbon fiber grade that are manufactured using isotropic pitches. These fibers are classified as non-graphitic and exhibit inferior qualities

compared to high-performance grade (HP) fibers, requiring mesophase pitch to be used (J. Yang et al., 2017). Pitch derived directly from the processing of crude oil is termed isotropic pitch, characterized by its immediate formation from the crude oil processing units. However, this form of pitch often requires further refinement to optimize its properties for practical applications. This enhancement involves reducing volatile components, fostering the formation of larger molecular structures through specific reactions, and diminishing the content of non-soluble solids, such as ashes. The following sections discuss the essential approaches utilized in the handling of isotropic pitch (Yuan et al., 2020).

2.4.1.1 Solvent Deasphalting (SDA)

In the solvent deasphalting (SDA) technique, light paraffinic solvents are used to produce asphaltene-rich pitch and higher-value deasphalted oil (DAO), which is the raw material for fluid catalytic cracking and also used in hydrocracking. Asphaltene is a fraction in heavy oil or bitumen that is characterized by its insolubility in n-alkane solvents, often n-pentane or n-heptane. In an industrial SDA process, heavy oil or bitumen is mixed with the chosen solvent to remove the insoluble n-alkane, which is considered refined pitch (isotropic pitch) and can be directly sent to the melt-spinning or need further preparation by the above-mentioned methods (Y. Lee et al., 2020; Shin et al., 2014).

Figure 10 represents a simplified solvent deasphalting unit designed to extract light fractions from petroleum pitch. The pitch is initially combined with a solvent in a mixer. The combination is subsequently directed into an extractor, wherein the lighter

constituents, referred to as maltenes, are segregated from the denser asphaltenes as a result of their distinct solubilities. The maltenes, which are currently referred to as the 'light product', are subsequently directed to the DAO stripper, where the solvent is extracted, leading to the formation of the 'DAO Product'. This product is then prepared for subsequent processing or utilization. Simultaneously, the substance referred to as the 'heavy product', specifically the asphaltenes, is directed towards the asphaltene separator in order to be gathered. Significant research endeavors are dedicated to the reduction of the solvent-to-pitch ratio, which currently spans from four to tenfold, as well as the optimization of solvent recovery in order to minimize energy consumption. This reduction in energy usage is of significant importance, as it accounts for a substantial proportion of the overall energy demand of the unit (Hamidi Zirasefi et al., 2016; Lodi et al., 2015).

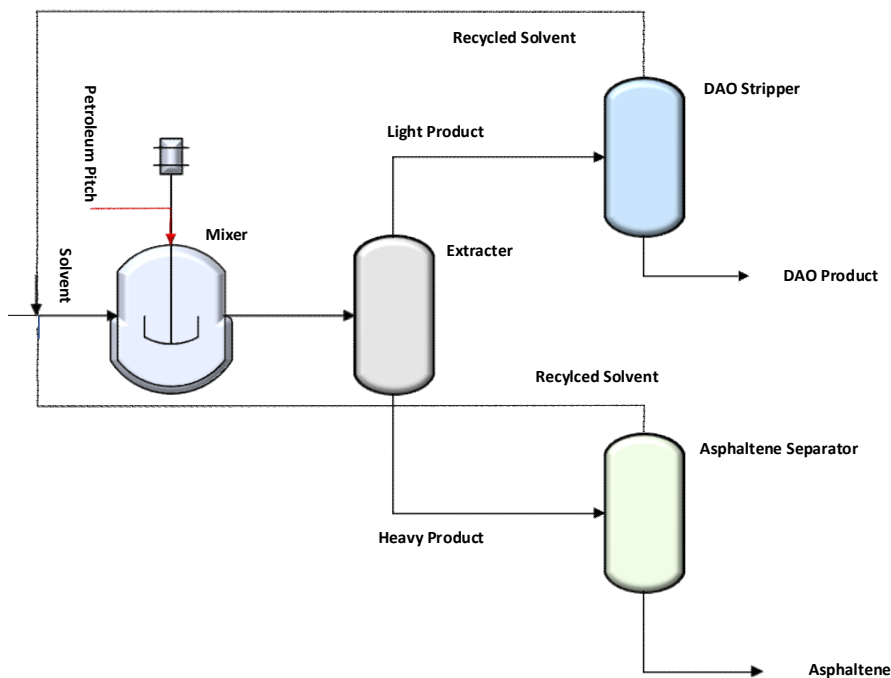


Figure 10. Simplified diagram of a solvent deasphalting unit used in the petroleum industry to separate heavy components (Lodi et al., 2015).

Table 2 summarizes the methods employed for the production of isotropic pitch from various petroleum pitches following SDA. Leandro Lodi et al. (2015) extracted 1% v/v DAO from vacuum residue using CO₂ as solvent. Using ethanol as a solvent, they obtained about 75% v/v DAO. Hexamethyldisiloxane (HMDSO) resulted in about 38.7% asphaltene from Ashalchinskaya heavy crude oil at an optimal HMDSO/oil ratio of 15/1. The use of n-heptane resulted in about 80.5% DAO yield. Kim (2021) comprehensively investigated the asphaltene yield from industrial *n*-C5-insoluble raw asphaltenes. The properties of *n*-C5 and *n*-C7 asphaltenes include elemental analyses, penetration, functional groups, aromaticity, and nickel and vanadium content. The removal of *n*-C7-soluble materials from industrial asphaltenes in the *n*-C5 solvent deasphalting process negatively impacted the melt spinning process, resulting in inconsistent fibers and low melt spin productivity. A crucial *n*-C7-soluble but *n*-C5-insoluble component is needed.

Table 2. compiles a number of studies that have contributed to the field of isotropic pitch production using the solvent deasphalting method.

Raw Materials	Solvents	Conditions	Features	Ref.
Vacuum residue (VR). Atmospheric residue (AR)	Carbon Dioxide	Pumping carbon dioxide occurs at 31.05 °C and 73.83 bar. Extraction conditions (78.83 bar, 250 bar, 300 bar, 110 °C, 135 °C) and extraction time were 60 min.	DAO extracted was around 1% v/v.	(Lodi et al., 2015)

Vacuum residue	Ethanol	Extraction Temperature ranged between 170 °C and 300 °C, pressure was 85–120 bar, and extraction time was 60 min.	DAO extracted was around 75% v/v.	(Lodi et al., 2015)
Ashalchinskaya heavy crude oil	Hexamethyldisiloxane (HMDSO)	HMDSO was mixed with oil at 60 °C. The extraction time is 24 hours.	The HMDSO/oil ratio is 15/1 (vol/vol), which gives a yield of 38.7% asphaltene.	(Ilyin et al., 2022)
Vacuum tower bottoms (VTB).	n-heptane	n-heptane is introduced at 4.45 bar, 75 °C extraction temperature, and 512 °C extraction time of 3 h.	80.5% DAO yield	(Ilyin et al., 2022)
Industrial n-C ₅ -insoluble raw asphaltenes	nC ₅	Solvent: raw asphaltenes 5:1	86.7 wt.% asphaltenes	(Y. Kim et al., 2021a)
		Solvent: raw asphaltenes 10:1	83.6 wt.% asphaltenes	
		Solvent: raw asphaltenes 40:1	80.6 wt.% asphaltenes	
Industrial n-C ₇ -insoluble raw asphaltenes	nC ₇	Solvent: raw asphaltenes 5:1	83.3 wt.% asphaltenes	(Y. Kim et al., 2021a)
		Solvent: raw asphaltenes 10:1	78.6 wt.% asphaltenes	
		Solvent: raw asphaltenes 40:1	72.3 wt.% asphaltenes	

The amount of asphaltene depends on the type and amount of solvent used. For n-alkanes as solvents, it also depends on the carbon number. The literature suggests that starting with bitumen as feed results in lower yields for n-C7 insoluble asphaltenes than n-C5 insoluble asphaltenes. It is important to optimize the deasphalting conditions based on the feed material and solvent used.

2.4.1.2 Autoxidation

Autoxidation is a type of oxidation reaction that occurs spontaneously in the presence of oxygen, without the need for a catalyst. It is a process where materials, typically organic compounds, are oxidized by atmospheric oxygen. It can be used to increase the viscosity of road paving asphalt, making it more resistant to weather and temperature changes. This process is a free radical chain process and can produce various final products like oxygenated compounds (peroxides, alcohols, carbonyl compounds, acids, esters, and/or cross-linked molecules), as shown in **Figure 11** (de Klerk, 2011).

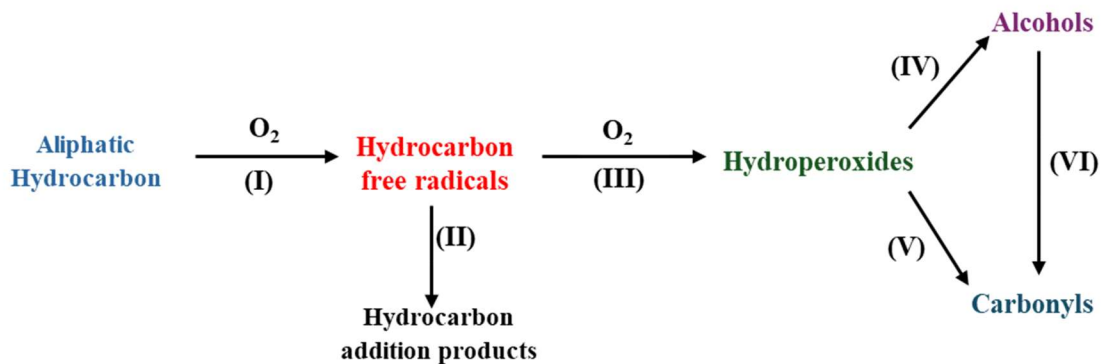


Figure 11. Overall reaction network of the aliphatic hydrocarbon autoxidation (Siddiquee & De Klerk, 2014).

The availability of oxygen is crucial in the chemistry of free radical oxidation, as it has a significant impact on the creation of free radicals through H-abstraction (initiation) and the subsequent propagation processes (**Figure 11**). If oxygen is present, the reaction for free radical formation proceeds to step III. However, if there is a lack of oxygen, the reaction progresses to the synthesis of a heavier product in step II (Muhammad Nurunnabi Siddiquee, 2014).

2.4.1.2.1 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, de Klerk, et al., 2016).

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).

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 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):



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 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 (6) (De Klerk, 2003):



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 7–9 (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 11**.

Autoxidation of heavy petroleum fractions is a valuable technique for applications like in situ recovery, road construction hardening, and upgrading heavy petroleum, as it induces chemical and physical changes, such as increased viscosity and asphaltene content. The naphthenic-aromatic hydrocarbon class may be responsible for bitumen hardening or viscosity increases. **Figure 12** demonstrates that naphthenic-aromatic hydrocarbons, particularly indene, tetralin, and indan, have a strong capacity for forming addition products during autoxidation, as evidenced by their high selectivity to addition reactions with increasing oxygen consumption (Siddiquee, De Klerk, et al., 2016a). Indene shows the highest selectivity, reaching nearly 30%, followed by tetralin and indan, which also display significant addition behavior. In contrast, compounds like n-decane, decalin, and p-cymene show minimal selectivity, indicating they contribute less to viscosity and hardness. Additionally, Siddiquee et al. conducted autoxidation experiments on tetralin at 130 °C for various reaction durations and observed that the color of tetralin progressively darkened to black over time, resulting from the formation of addition products (**Figure 13**), this data supports the idea that naphthenic-aromatic hydrocarbons can play a critical role in enhancing the physical properties of heavy petroleum fractions through addition reactions, leading to hardened, and more viscous materials (Siddiquee & De Klerk, 2014), that might be suitable for carbon fiber precursors

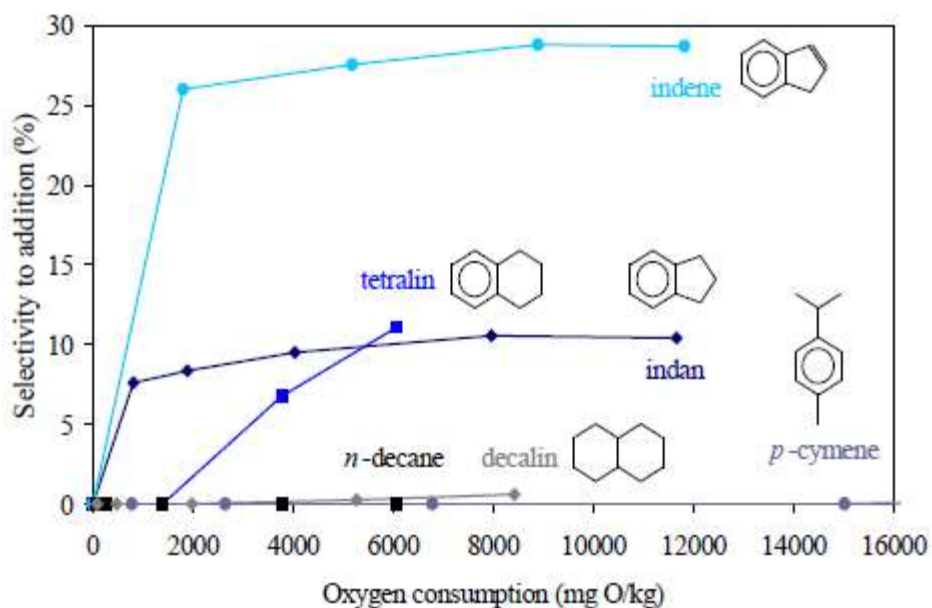


Figure 12. Selectivity to addition products during the autoxidation of model compounds at 130 °C (Siddiquee & De Klerk, 2014).

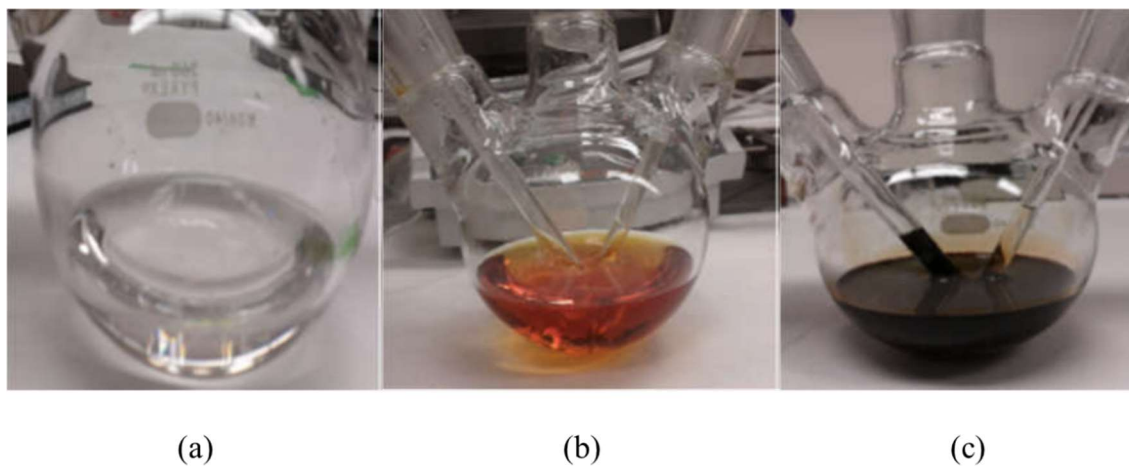


Figure 13. (a) Tetralin; (b) tetralin oxidized at 135 °C for 24 hour and (c) tetralin oxidized at 150 °C for 48 hours (Siddiquee & De Klerk, 2014).

Table 3 highlights a variety of research efforts on isotropic pitch precursor formation via autoxidation. For instance, studies have demonstrated that under certain conditions, such as air blowing at 330 °C with a 5–15 wt. % DNN additive, the softening point of the

naphthalene pitch can be improved significantly. Another example includes the autoxidation of quinoline insoluble (QI) pitch at temperatures between 280 and 320 °C, which resulted in a pitch with a high softening point of 280 °C and a high coking value, indicative of its suitability for carbon fiber production. These examples illustrate the tailored approaches to modifying pitch properties that are critical for the advancement of carbon fiber technologies.

Table 3. A comparative summary of autoxidation conditions and outcomes for petroleum pitch in carbon fiber precursor studies.

Raw Materials	Conditions	Features	Ref.
Asphaltenes	Autoxidation 190–250 °C	A slight change in Young’s modulus increase in melt spin productivity For asphaltenes, penetration depth decreased from 15.3 ± 0.4 mm to 3.4 ± 1.1 mm.	(Y. Kim et al., 2021a)
Aromatic petroleum feedstock	Batch-wise oxidation at 315–371 °C, air flow rate up to 0.2 cfm/bbl.	Softening point: 99–121 °C Benzene insoluble: 25– 35%	(Marc Michael Seinfeld, 1974)
Petroleum pitch (Ashland A 240)	1 MPa of oxygen pressure. Temperatures between 200 and 280 °C	Formation of oxygenates and cross-linking among oxygenates	(Metzinger & Hüttinger, 1997)
Isotropic naphthalene and hydrogenated coal tar pitches	Air blowing at 330°C with 5–15 wt% DNN: control of reaction conditions, including temperature and blowing atmosphere.	Softening point of naphthalene pitch: 200– 210 °C Softening point of hydrogenated coal tar pitch: 275°C	(Zeng et al., 1993)

1,8-dinitronaphthalene (DNN) additive			
Coal tar pitch Petroleum feedstocks	Air blowing temperature: 330°C, 360°C, 380°C; air blowing duration: 35 to 265 minutes	increased softening point approximately by 80 °C Improved spinnability (12 to 14 µm dia)	(Maeda et al., 1993)
Quinoline- insoluble (QI) pitch	Air blowing temperature: 280–320 °C Thermal treatment temperature: 350-380 °C	High softening point (280 °C) and high coking value (82%)	(Yu et al., 2012)
Pyrolysis fuel oil (PFO)	700 g PFO, 1 L reactor, temperature of 360 °C, 5 h air flow rate of 0.5L/min, vigorous mixing.	The softening point changed from 130 to 249 °C.	(Ko et al., 2017)
High-purity impregnant asphalt serves as the raw material.	Reaction temperature: 280–300 °C, with air. Devolatilization temperature: 260–300 °C	Softening point: 115–125 °C. Quinoline undissolved substance content: 0.5– 2%.	(Liu Yue, Zhang Wenchang, Han Bo, 2017)

The use of autooxidation for pitch pretreatment in the production of carbon fiber precursors poses challenges in terms of controlling and regulating the reaction's rate, maintaining precise temperatures to prevent the formation of unwanted byproducts, handling the higher viscosity of oxidized pitch, and ensuring scalability while achieving a precursor quality that is suitable for fiber spinning (Sh et al., 2020).

2.4.1.3 Halogenation/Dehalogenation

A common pretreatment methodology in the fabrication of carbon fiber precursors involves applying halogenation and then dehalogenation. The technique includes the incorporation of halogen elements (e.g., fluorine, chlorine, bromine, or iodine) into the organic compounds of the initial substance, commonly a pitch or a polymer. Following the halogenation process, the precursor dehalogenates, eliminating the halogen atoms and forming a free radical. This free radical is then available for subsequent addition reactions, as shown in **Figure 14** (Mochida et al., 1988).

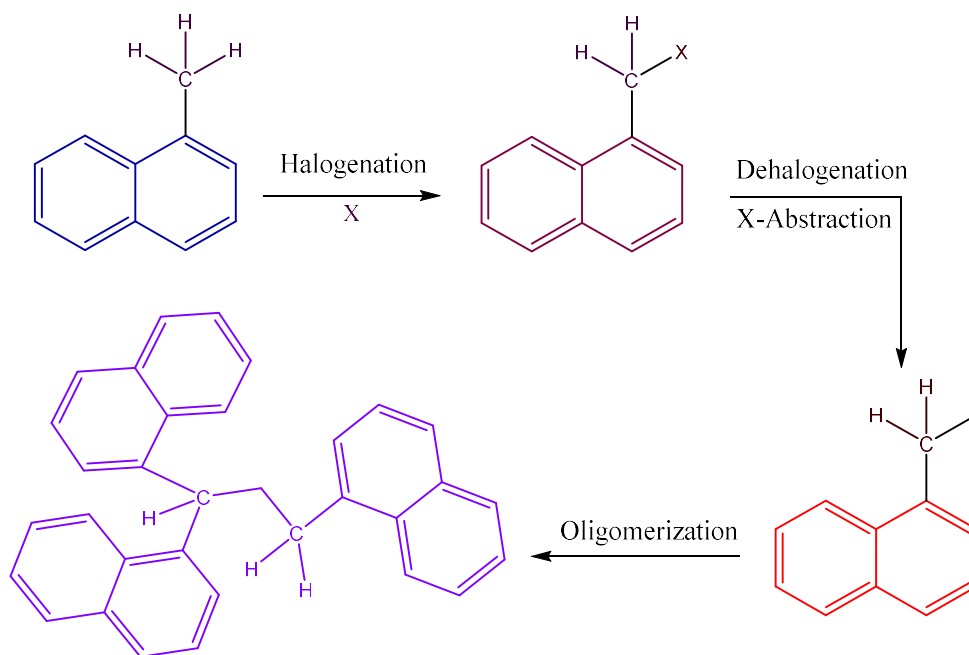


Figure 14. This figure shows how an aromatic molecule (methyl naphthalene) goes through halogenation and then dehalogenation (J. Liu et al., 2023).

Based on the specific halogen involved, this technique may be termed fluorination-defluorination, bromination-debromination, or chlorination-dechlorination, reflecting the

respective addition and removal of fluorine, bromine, and chlorine atoms from the target molecules. The processes of fluorination and defluorination are utilized specifically in the synthesis of mesophase pitch, which will be covered in the Preparation of Mesophase pitch section. By replacing a hydrogen atom in an aromatic ring with a bromine radical and removing the hydrogen bromide at 300 °C, a chemical process known as bromination-debromination creates aromatic compounds via side chain bridge bonds. **(Figure 14)** (Liang et al., 2020). This process features moderate cost and mechanical performance, is simple to control and operate with relatively weak corrosion to equipment, but has low reactivity, leading to large additions and moderate toxicity (B. J. Kim et al., 2016).

Similar to bromination-debromination, which also uses chlorine radicals to start free radical chain reactions, the mechanism of the chlorination/dechlorination process works. Chlorine radicals can be produced by a homolytic process from chlorine gas or by the thermal degradation of polymers containing chlorine, such as polyvinyl chloride. Chlorinated aromatic hydrocarbons are created when the side chain of the aromatic ring's hydrogen is replaced by chlorine radicals. During dechlorination, the hydrogen atoms on other aromatic molecules mix with the chlorine atoms on the chlorinated aromatic hydrocarbons as the reaction temperature rises to generate hydrogen chloride, which is subsequently removed from the reaction system by passing an inert gas. To guarantee total removal, the chlorine gas in the reaction system can alternatively be removed using a vacuum followed by air. Alternatively, air can flow into the reaction system simultaneously. This process is simple to regulate, moderately expensive, and has low additions and mechanical performance; on the other hand, it has moderate toxicity

problems and strong equipment corrosion hazards (J. Liu, Shimanoe, Nakabayashi, Miyawaki, Choi, et al., 2018).

Referring to **Table 4**, studies on isotropic pitch precursor formation using halogenation show varied conditions and outcomes. For instance, bromination of a biotar and ethylene bottom oil mixture at 110 °C with 20% Br₂, followed by dehydrobromination at 320 °C under N₂, led to a softening point of 205 °C and a tensile strength of 1200 MPa. Chlorination and dehydrochlorination of ethylene bottom oil (EO) mixed with polyvinyl chloride (PVC) up to 350 °C yielded a durable pitch with no breakage under extreme winding. Aromatic-rich distillate oil co-carbonized with polyvinyl alcohol (PVA) at 390 °C for 8 hours resulted in a softening point of 281 °C, and pitch processed with bromine at 420 °C for 9 hours achieved a softening point of 297 °C and high tensile strength, underscoring the diverse methodologies for enhancing isotropic pitch properties for carbon fiber precursor development.

Table 4. Different halogenation conditions and their outcomes for producing isotropic pitch, an essential precursor in carbon fiber manufacturing.

Raw Materials	Halogen used	Conditions	Features	Ref.
Biotar and ethylene bottom oil mixture Br ₂ (bromine) addition	Bromine	Bromination: 110°C for 1 hour, 20% Br ₂ Dehydrobromination: 320°C for 3 hours under N ₂	The softening point is 205 °C. Tensile strength of 1200 MPa	(J. Yang et al., 2017)
Ethylene bottom oil (EO) and polyvinyl chloride (PVC)	Chlorine	Chlorination-dehydrochlorination: (230 °C–310 °C) co-carbonization reaction: at temperatures up to 350 °C	Up to 1200 rpm, the pitch demonstrated nearly no pitch fiber breaking even under extremely harsh winding conditions (the spun fiber diameter was about 8 μm).	(J. Liu, Shimanoe, Nakabayashi, Miyawaki, Ko, et al., 2018)

Aromatic-rich distillate oil (HCTO) and polyvinyl alcohol (PVA)	Chlorine	The co-carbonization reaction was carried out at 390 °C for 8 hours. Adding 5% (wt%) of PVA	The softening point is 281 °C. The spinning temperature is 281 °C.	(Luning Chai, 2023)
Fluidized catalytic cracking-decant oils (FCC-DO)	Bromine	The PM pitch was heated at 420 °C for 9 hours.	Softening point of 297 °C; tensile strength of 750 MPa at 1200 °C carbonization	(Park et al., 2001)

In the arena of carbon fiber production from isotropic pitch, heat treatment often stands as the foundational pretreatment step. This method primes the pitch for subsequent advanced refining processes, such as solvent deasphalting, autoxidation, and halogenation/dehalogenation. According to all the research that has been done, heat treatment alone can change the pitch in some good ways, but it is usually needed with other methods to get the best precursor quality for general-purpose (GP) carbon fiber manufacturing. These combined approaches aim to reduce volatile content, encourage polymerization, and eliminate non-soluble solids, thereby enhancing the pitch's suitability for carbon fiber production (J. Yang et al., 2017).

Despite the challenges inherent in processing isotropic pitch, such as high viscosity and complex molecular content, the integration of heat treatment with other methods illustrates the industry's commitment to innovation. Each method carries its own trade-offs concerning cost, operational complexity, and environmental impact, which must be judiciously managed. The end goal remains consistent: to produce cost-effective, high-quality carbon fibers while ensuring the process's feasibility and sustainability.

2.4.2 Preparation of Mesophase Pitch Precursor

Mesophase pitches are critical in producing high-performance carbon fibers, which are desired across various sectors for their exceptional strength-to-weight ratio and stiffness. Unlike isotropic pitches, which yield fibers with more random molecular orientation and thus lower mechanical properties, mesophase pitches result in fibers with a highly oriented structure, as shown in **Figure 15**, leading to superior tensile strength and modulus. Pretreatment technologies for mesophase pitch are crucial in the production of high-performance (HP) carbon fibers, as they initiate polycondensation and polymerization reactions that align aromatic hydrocarbons into discotic mesogens. This alignment is essential for mesophase formation, impacting the crystalline structure and enhancing the potential for graphitic ordering during subsequent heat treatments. Effective viscosity control is key during this stage; it decreases to improve fluidity as mesogens align and then increases with the mesophase content, reflecting greater molecular order. This controlled viscosity is vital for ensuring smooth extrusion through spinnerets during melt-spinning (D. Liu et al., 2016).

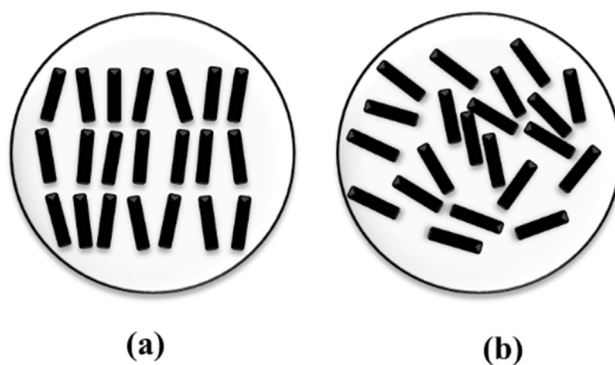


Figure 15. Illustration of molecular orientation in pitch materials: (a) mesophase pitch and (b) isotropic pitch (Klimenko, 2022).

Pyrolysis is a fundamental process in the production of mesophase pitch, serving as the thermal decomposition method for transforming organic materials into mesophase structures suitable for carbon fiber production. During pyrolysis, organic materials are subjected to high temperatures in an oxygen-free environment, leading to their breakdown into smaller, reactive species. These reactive molecules, rich in aromatic compounds, act as building blocks, termed "mesogens," which reorganize into planar, ordered structures characteristic of mesophase pitch. As the pyrolysis process advances, these mesogens undergo further polymerization and condensation, fostering the growth and development of mesophase domains. This progression is critically dependent on tightly controlled pyrolysis parameters, including temperature, heating rate, and duration. Such control is vital to prevent the pitch from merely carbonizing into a non-melting solid but instead forming a structured, spinnable mesophase capable of being processed into high-quality carbon fibers. Reflecting the effectiveness of pyrolysis in producing mesophase pitch for carbon fiber, **Table 5** highlights various studies that demonstrate how specific pyrolysis conditions influence the characteristics of mesophase pitch. For instance, pyrolysis fuel oil (PFO) treated at 420°C–430°C achieves a 95wt% mesophase content with a softening point of 279°C, emphasizing the role of high-temperature treatments in promoting mesophase formation and enhancing thermal properties. Similarly, synthetic asphalt ethylene bottom oil pitch processed between 350 and 400 °C yields a 70 wt. % mesophase content and a softening point of 220 °C. These examples underline the critical importance of carefully controlled pyrolysis settings to optimize mesophase content and properties, crucial for the successful production of high-quality carbon fibers.

Beyond pyrolysis, solvent extraction is a noteworthy additional essential process for mesophase pitch production. Using particular solvents, this method dissolves some pitch components, concentrating on eliminating non-mesophase materials to add mesophase-forming compounds. Under more thermal processing, the big, planar target aromatic molecules realign to create a liquid crystalline mesophase (Popova et al., 2022).

Another method, hydrogenation, involves adding hydrogen to the pitch in the presence of a catalyst. This technique diminishes the aromatic structures of the pitch, resulting in alterations to its characteristics (Phiciato et al., 2023). Through the addition of hydrogen, the pitch undergoes a reduction in aromaticity and an increase in hydrogen content, resulting in a modification of its molecular composition. This alteration induces the reorganization of pitch molecules, hence facilitating the creation of mesophase structures. The presence of these structures is crucial in the production of carbon fibers of superior quality since they possess a highly organized configuration that enhances the strength and performance of the fibers (Azami et al., 1993). The primary challenge in using hydrogenation for mesophase pitch formation is precisely controlling the hydrogenation process to avoid oversaturation, which can hinder the development of the desired mesophase structure (Wang et al., 2023).

Additionally, catalytic polymerization further extends the capabilities of mesophase pitch production by polymerizing compounds like naphthalene using catalysts to encourage the formation of mesophase structures. This method requires strict control of the polymerization process to achieve the desired mesophase properties without unwanted byproducts (P. Y. Yang et al., 2018).

Table 5. Methods for converting various petroleum pitches into mesophase pitches.

Raw Material	Method used	Process Conditions	Product Properties	Ref.
Pyrolysis fuel oil (PFO)	Pyrolysis	heat treatment at 420°C–430°C for 2.5 h under autogenous pressure. carbonization at 800 °C, and graphitization at 2400 °C.	Mesophase content: 95 wt% Softening point: 279°C Tensile Strength: 1.9–2.7 GPa Young's modulus: 554–635 GPa	(Tomaru et al., 2024)
Synthetic asphalts ethylene bottom oil pitch hybrid	Pyrolysis	Temperature: 350–400 °C for 2–30 h, flash distillation under a 0.1 MPa vacuum atmosphere. Carbonization: 600–1400 °C for 0.25-2 h; graphitization: 2200–3000 °C for 0.25-2 h	Mesophase content: 70 wt% Softening point: 220°C Tensile Strength: 1.5–4.0 GPa Young's modulus: 300–600 GPa Thermal conductivity: 500–800 W/mK. electrical resistivity is less than 0.2×10^{-10} $\Omega \cdot \text{cm}$,	(Xinhua & Rui, 2016)
Quinoline-insoluble (QI) pitch	Solvent extraction	The solvent used to extract QI was treated at 440 °C for 4 hours.	Mesophase content: 19.9%. The average sphere radius is 4.5–100 μm .	(Lai et al., 2012)
Isotropic naphthalene pitch	Fluorination-defluorination	Reaction Temperature: 210–300 °C. Reaction time: 4 hours HF–BF ₃ catalyst under 2.1 MPa	Yield of 0.8–0.9 and a softening point of 285 °C. Its solubility in benzene and quinoline was as high as 42 and 74%, respectively.	(Mochida et al., 1992)
Pyrolysis fuel oil (PFO)	Solvent Hydrogenation	0.33–1.50 wt%. PET (polyethylene terephthalate) is used as a solvent. N ₂ gas flows at 200 mL/min for 40 min to prevent oxidation. Temperature: 400 °C, and time: 300 min.	Softening points of 196 °C. Mesophase content: 38%. Overall yield: 24.9%.	(J. H. Kim et al., 2021)

Fluidized catalytic cracking-decant oil (FCC-DO)	Catalytic Hydrogenation	Using a zeolite catalyst, the reaction temperature is 400 °C, and the reaction time is 240 min.	Softening points of 350 °C, viscosity at 150 °C is 153.7 cP, and mesophase yield is 36.4%.	(D. H. Lee et al., 2017)
Ethylene, tar, and naphthalene	catalytic polymerization	trifluoride diethyl etherate as a catalyst, reaction pressure: 6-3 MPa. Temperature: 380~400 °C under a nitrogen atmosphere for 5 hours.	Softening points of 270°C Mesophase content: 100%.	(He et al., 2024)

In the area of mesophase pitch formation, numerous patents have been granted for processes that either utilize the primary techniques mentioned above, combine them, modify conditions, or add additives, often under diverse terminologies. For instance, conducting pyrolysis in the presence of air can be referred to as thermal polycondensation, similar to autoxidation but under more severe conditions (Qu et al., 2022). Similarly, the method of hydrogenation, when employing hydrogen donor solvents, is termed solvent hydrogenation, and if a catalyst is added to this mix, it is known as catalytic hydrogenation. The introduction of fluorine-containing compounds like HF and BF₃ (Lewis acid) into the process is labeled as the fluorination/defluorination process. While these are variations of the main techniques, the foundational methods of pyrolysis, solvent extraction, catalytic polymerization, and hydrogenation remain central and pivotal in mesophase pitch production.

The various methods and raw materials detailed in **Table 5** illustrate the intricate processes involved in forming mesophase pitch, a crucial precursor for high-performance carbon fibers. Techniques such as solvent extraction, hydrogenation, and catalytic polymerization, each tailored to specific raw materials like quinoline insoluble pitch, pyrolysis fuel oil (PFO), and ethylene tar, demonstrate varying mesophase content and mechanical

properties upon treatment under specific conditions. For instance, catalytic polymerization of ethylene tar and naphthalene using trifluoride diethyl ether achieves a 100% mesophase content and a softening point of 270 °C, showcasing the effectiveness of precise catalytic methods in promoting structured mesophase formation. Each method and condition set in the table underscores the need for strategic control over process parameters to optimize the mesophase content and achieve desired material characteristics suitable for advanced carbon fiber applications.

Quantifying mesophase content is essential for controlling the quality of mesophase pitch and the performance of the resulting carbon fibers. Techniques such as Polarized Light Microscopy (PLM), which identifies mesophase through its characteristic anisotropic textures like maltese crosses, and Scanning Electron Microscopy (SEM), which provides detailed microscale images of mesophase structure, are commonly employed. Additionally, X-Ray Diffraction (XRD) offers insights into the crystalline structure, indicating the orientation and graphitic ordering within the mesophase. Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy, particularly ^{13}C NMR, identifies structural changes in carbon atoms during the isotropic to mesophase transition. Differential Scanning Calorimetry (DSC) measures phase transition-related heat flows, and rheological measurements assess flow behavior and viscosity changes due to mesophase content. These methods, often used in combination, provide a comprehensive analysis necessary for optimizing mesophase pitch preparation and processing for carbon fiber production (Li et al., 2015).

2.5 Environmental and Sustainability Considerations

Environmental and sustainability considerations are integral to assessing the feasibility of carbon fiber production from heavy oil or heavy petroleum fractions. A critical component of this evaluation is a life cycle analysis (LCA), which provides insights into environmental impacts across all stages of the process. The energy-intensive nature of carbon fiber production, especially in heavy oil-based processes during carbonization, raises concerns about greenhouse gas emissions. Effectively managing waste and byproducts generated in the carbon fiber production process is a significant challenge that requires attention to minimize environmental impact.

Evaluating the environmental impact of carbon fiber production from heavy petroleum fractions necessitates a comprehensive analysis across various production stages. Sakib et al. (2024) highlight the significance of LCA as a crucial tool, emphasizing its role in identifying environmental hotspots and guiding targeted improvements throughout the entire life cycle of the process (Sakib et al., 2024; Salim et al., 2018). The energy-intensive nature of carbon fiber production raises concerns about greenhouse gas emissions, and optimizing energy efficiency as well as exploring renewable energy sources is essential for mitigating environmental impact, as discussed by Keboletse et al. (2021) (Keboletse et al., 2021).

Al Bari et al. (2023) studied the techno-economic and LCA of asphaltene-derived carbon fiber (ACF) production, aiming to assess its economic and climate benefits. Their analysis suggests that production costs can remain below \$9 per kg of ACF due to the cost-effective asphaltene precursor. Energy reduction during high-temperature carbonization could further cut costs and show potential climate benefits, with the lowest global warming

potential (GWP) among compared precursors. Asphaltene extraction during bitumen partial upgrading emerges as the most energy-intensive phase, influencing environmental impacts (Bari et al., 2023). Baritto et al. (2023) devised data-intensive models to gauge the life cycle greenhouse gas (GHG) emissions of ACF, conducting sensitivity and uncertainty analyses to pinpoint influential inputs. Their findings reveal that ACF's life cycle GHG emissions stand at 16.2 kg CO₂eq/kg CF, marking a notable 68.7% reduction compared to PAN-based carbon fiber. In another study, a techno-economic assessment of ACF production from bitumen was conducted to estimate production costs using developed process models. Data on material and energy requirements, main equipment sizing, and capital and operating costs were obtained from a comprehensive process model. Findings indicate that at a plant capacity of 3,000 tons per year, the production cost amounts to \$10.16 per kg of carbon fiber (Baritto et al., 2023)(Groetsch et al., 2021). Further discussion on LCA can be found in the literature (Sakib et al., 2024; Salim et al., 2018).

Current developments in recycled carbon fibers and carbon recyclates (derived from the recycling of carbon fiber-reinforced composites) are also pivotal to advancing the sustainability of carbon fiber production. For instance, Pimenta and Pinho (2011) explore innovative recycling methods for carbon fiber composites, aiming to reduce environmental impact and enhance the lifecycle of carbon fibers. This study demonstrates that recycled carbon fibers retain much of their mechanical strength and can be effectively used in various applications, thus reducing the need for virgin carbon fibers and lowering overall emissions (Pimenta & Pinho, 2011). Moreover, the integration of carbon recyclates in new composite materials highlights potential pathways for achieving circular economy goals in the carbon fiber industry. Research by Oliveux et al. (2015) reviews different recycling

technologies, including mechanical, thermal, and chemical methods, emphasizing the importance of developing cost-effective and efficient processes to facilitate wider adoption of recycled carbon fibers (Oliveux et al., 2015).

Further directions for research include the optimization of recycling processes to improve the quality and performance of recycled carbon fibers. For example, studies on the chemical recycling of carbon fibers using solvolysis (Zhang et al., 2024). have shown promising results in retaining fiber strength and reducing environmental impact. Additionally, advancements in the pyrolysis process, as reviewed by Naqvi et al. (2018), could enhance the economic viability and environmental performance of recycling carbon fiber composites (Naqvi et al., 2018).

Another significant direction is the integration of renewable energy sources into the production and recycling processes. As suggested by Huang et al. (2024), utilizing solar and wind energy for the high-temperature processes involved in carbon fiber production can substantially reduce the carbon footprint (Huang et al., 2024). Research on the co-pyrolysis of biomass and plastic waste with carbon fibers (Seah et al., 2023). also indicates potential for creating sustainable composite materials. Moreover, developing robust policy frameworks and industry standards to support the use of recycled carbon fibers can drive market adoption and innovation. The study by Gopalraj and Kärki (2020) highlights the role of government incentives and regulations in promoting sustainable materials in the composites industry (Karuppannan Gopalraj & Kärki, 2020).

Overall, the environmental and economic feasibility of carbon fiber production from heavy petroleum fractions can be significantly enhanced through comprehensive LCA, optimization of energy use, advancements in recycling technologies, and integration of

renewable energy sources. Continued research and development in these areas, supported by strong policy frameworks, are essential for achieving sustainable carbon fiber production.

2.6 Research Gaps in Utilizing Heavy Petroleum Fractions for Carbon Fiber Production

1. **Detailed Chemical Composition and Impurity Analysis:** Current research lacks comprehensive insights into the detailed chemical composition of heavy petroleum fractions, including impurities and their variations. A deeper understanding of these components is essential for optimizing pretreatment processes, ensuring consistent quality, and improving the overall efficiency of carbon fiber production from these heavy fractions.
2. **Mass Transfer and Reaction Engineering Fundamentals:** There is a need for more focused studies on the reaction engineering and mass transfer aspects crucial to developing a cost-effective and sustainable pre-treatment method. Specifically, understanding the impact of factors like mixing, gas-liquid interfacial area, and oxygen transfer rates on autoxidation and other chemical processes would enhance control over the creation of stable, carbon-rich materials.
3. **Role of Naphthenic-Aromatic Compounds in Autoxidation:** Research has yet to fully explore the role of naphthenic-aromatic compounds, such as tetralin, in promoting addition reactions and forming olefin products during autoxidation.

Investigating these additives could be essential for enhancing the quality and yield of carbon fiber precursors from heavy petroleum fractions.

4. **Strength Enhancement of Petroleum-Based Carbon Fibers:** Increasing the strength of petroleum-derived carbon fibers remains a complex challenge, especially for structural applications. Research on carbon composite lattice design, specifically for applications like hydrogen storage, pipelines, and construction, is limited. Exploring fabrication techniques, such as 3D weaving, could impart tailored properties suited to different applications.
5. **Environmental and Sustainability Considerations:** Although some studies touch on sustainability, there is an absence of a comprehensive life cycle assessment to evaluate the environmental impact of heavy petroleum fraction-based carbon fiber production. A holistic approach is needed to address ecological concerns and promote sustainable practices throughout the production process.
6. **Economic Feasibility of Large-Scale Production:** Few studies provide a thorough economic analysis of large-scale carbon fiber production from heavy petroleum fractions, including factors like production costs, scalability, and market competitiveness with traditional precursors. Addressing these economic considerations would provide valuable insights into the viability of scaling up this innovative approach.

CHAPTER 3

MATERIALS AND METHODS

3.1 Material

In this study, two different feedstocks are heavy vacuum gas oil (HVGO) and vacuum residue (VR) were sourced from a local provider in Saudi Arabia and handled under controlled conditions to prevent premature oxidation. Both materials were stored in sealed containers and kept in a dark environment to limit exposure to light and reduce the risk of photooxidation, where light and oxygen can initiate free radical reactions, accelerating oxidation.

The heavy vacuum gas oil (HVGO) used in this study exhibits the following properties (as detailed in **Table 6**): it is predominantly composed of saturates (42.91 wt.%), aromatics (51.18 wt.%), and resins (5.90 wt.%), with no asphaltenes. The elemental composition includes high carbon (85.3 wt.%) and hydrogen (11.9 wt.%) content, along with minimal oxygen (0.4 wt.%) and nitrogen (0.1 wt.%). The viscosity of HVGO is 2.854 Pa.s at 25 °C and 0.730 Pa.s at 40 °C, while its density is measured at 1120 kg/m³, with a softening point of 37 °C.

The vacuum residue (VR), the heaviest fraction from vacuum distillation, contains significant amounts of high molecular weight hydrocarbons and impurities like sulfur, nitrogen, and metals. According to SARA analysis, VR contains no saturates but has a high

aromatic content (66 wt.%), resins (15 wt.%), and asphaltenes (20 wt.%). Elementally, VR is composed of approximately 82 wt.% carbon, 9 wt.% hydrogen, 1.5 wt.% nitrogen, 0.4 wt.% oxygen, and 6.9 wt.% sulfur. The softening point of VR is 54 °C.

Table 6. Composition and properties of feed HVGO and VR.

Property	HVGO	VR
SARA fractions (wt.%)		
saturates	42.91	0
aromatics	51.18	65.96
resins	5.90	15.07
asphaltenes	0	19.97
Elemental analysis (wt.%)		
Carbon	85.3	81.95
Hydrogen	11.9	9.29
Nitrogen	0.1	1.51
Oxygen ^a	0.4	0.38
Sulfur	2.3	6.87
Viscosity, Pa.s ^b .	2.85 ± 0.11	-
Viscosity, Pa.s ^c .	0.73 ± 0.01	-
Density, kg/m ³	1120	-
Softening Point, °C	37	54

^a Content was obtained by the difference.

^b Measured at 25 °C and average of 10 different values ± one standard deviation of a single sample.

^c Measured at 40 °C and average of 10 different values ± one standard deviation of a single sample.

The compressed nitrogen and zero-air gases with purity > 99.99% were procured from Air Liquide Gases, Saudi Arabia. Other chemicals such as tetralin (purity $\geq 99.8\%$), n-heptane (purity $\geq 99.8\%$), chloroform ($\geq 99.8\%$), acetone ($\geq 99.8\%$), toluene ($\geq 99.7\%$), hydrochloric acid (36%), sulfuric acid (98%), and nitric acid (86%), benzene (99.7%), and carbon disulfide (99.9%) are procured from Sigma-Aldrich.

3.2 Equipment Setup and Procedure

3.2.1 Autoxidation

HVGO and VR were autoxidized using the apparatus illustrated in Figure 16. The setup consisted of Pyrex round-bottom flasks with capacities of 250 mL and 500 mL, each equipped with three necks: one for air inlet, one for volatile vapor outlet, and one for a thermocouple. Temperature control and mixing within the flasks were maintained using a Heidolph MR Hei-Standard heat-on-block heater, which included a magnetic stirrer set to a constant 200 rpm. A gas flow meter (PMR 1-010977, Aalborg Instrument, USA) regulated the airflow rate to 152 mL/min from a compressed air cylinder into the petroleum fractions. Volatile vapors exiting through the second neck of the flask were rapidly

condensed in a borosilicate glass coil condenser, cooled by water maintained at 8 °C.

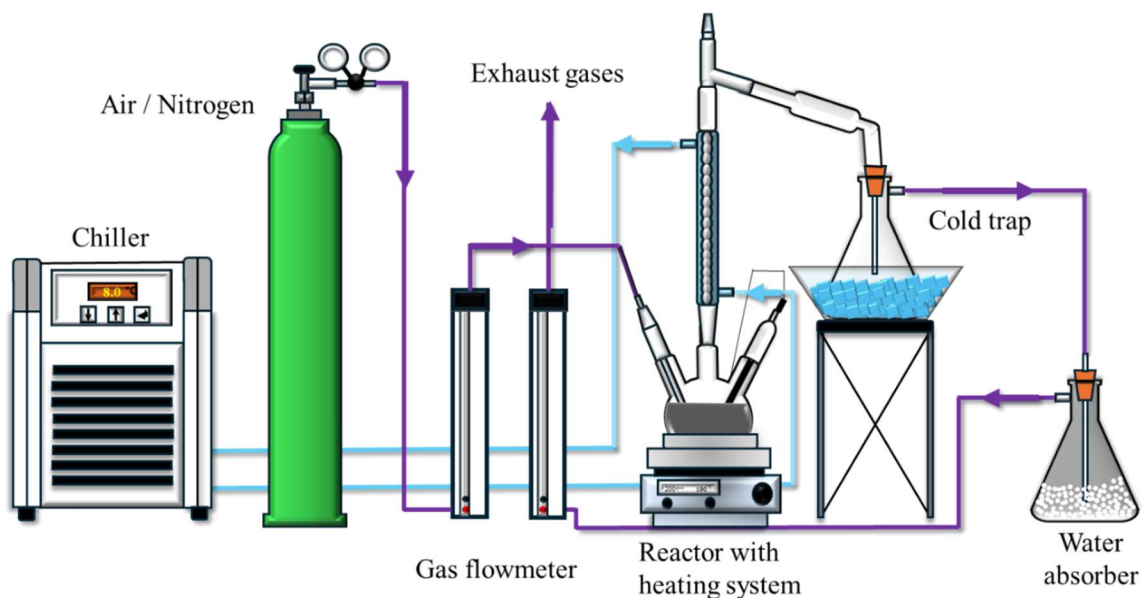


Figure 16. Schematic of experimental setup utilized in HVGO and VR autoxidation.

For each experiment, approximately 50-75 g of feedstock was loaded into the flask and heated to the desired temperature from 160°C or 280°C using the heat-on-block system, and a small amount of silicone oil was applied to improve contact between the glass and metal surfaces. Tetralin was added to the feedstock in varying concentrations (0 to 30 wt.%), and once the target temperature was achieved, the air supply was opened. Stirring continued at 200 rpm to ensure effective mixing, as the viscosity of the HVGO and VR at reaction temperatures were sufficiently low. Reaction times were set between 24 and 240 hours. After the completion of the experiment, the air supply was shut off, the apparatus was disassembled, and the final product was weighed to check the mass balance.

3.2.2 Melt Spinning

Melt spinning of the oxidized HVGO and VR and asphaltenes derived oxidized HVGO and VR samples was conducted using a melt-spinning machine (Model No. AT225) to produce "green fibers." A monofilament spinneret with a 150 μm diameter was utilized for the procedure. Approximately 10 g of the material was placed into the cylindrical heating chamber, which was then sealed. The material was heated until it reached its melting point, and the N_2 pressure was increased to 250 kPa to assess whether filaments would emerge from the spinneret. If no filament formed, the temperature was incrementally raised by 10 $^{\circ}\text{C}$, and the N_2 pressure was adjusted accordingly. This process continued until filaments were successfully produced. Once filament formation began, the winding process was started at a speed of 200-500 rpm by engaging the cycloid mechanism, aligning the polymer chains, and winding the filaments onto spools.

3.2.3 Acid Treatment

In order to activate the surface of green carbon fiber, the acid treatment was performed. In this process, the green carbon fiber was immersing into a 40% HNO_3 solution. The experiment was performed for 20 minutes at room temperature.

After acid treatment, the oxidative stabilization and carbonization of the treated sample was conducted using a compact split tube furnace (OTF-1200X-S50). The tube was made of quartz material with an outer diameter of 5 cm, 4.4 cm inner diameter, and 60 cm length.

3.2.4 Oxidative Stabilization

To prevent material fusion and sustaining the material structure at higher temperatures, the treated green fiber was oxidized. During the experiment, the air flow rate was set at 150 mL/min. The following procedure has been adopted to perform the experimental run:

The acid-treated green fibers were placed inside an alumina crucible, which was then positioned in the center of the furnace tube. The furnace program for oxidation, conducted in an air atmosphere, was set as follows: the temperature was increased from 0 to 150 °C at a rate of 3 °C/min, held for 10 minutes at 150 °C, then further raised from 150 to 300 °C at a rate of 5 °C/min, with a 24-hour hold at 300 °C. After this, the furnace was cooled from 300 to 150 °C at 5 °C/min, followed by a final cooling phase from 150 °C to 20 °C at a rate of 3 °C/min. Once the process was completed and the furnace had cooled down, the crucible was carefully removed using a long wire, and the resulting carbon fiber was collected for subsequent carbonization.

3.2.5 Carbonization

In order to avoid oxidation at higher temperatures to produce stabilized commercial carbon fiber, the heteroatoms present in the structure of carbon fiber were eliminated using carbonization. To avoid the oxidation of carbon fiber, inert environment was maintained throughout the experiment, where nitrogen gas flow rate was kept fixed at 150 mL/min. The following procedure had been adopted to perform the experimental run:

The oxidized fibers were placed inside an alumina crucible, which was then positioned in the center of the furnace tube. The furnace program for carbonization, under a nitrogen

(N₂) atmosphere, was set as follows: the temperature was gradually increased from 0 to 450 °C at a rate of 10 °C/min, held for 10 minutes at 450 °C, then further increased from 450 to 800 °C at a rate of 5 °C/min, with a 30-minute hold at 800 °C. Following this, the furnace was cooled from 800 to 450 °C at 5 °C/min, and finally cooled to 20 °C at a rate of 10 °C/min. After cooling, the crucible was carefully removed from the furnace using a long wire, and the resulting carbon fiber was collected for further analysis.

3.3 Analyses

3.3.1 SARA analysis

The weight% of saturates, aromatics, resins, and asphaltenes were computed using a combination of solvents and chromatography techniques. The sample was dissolved in a non-polar solvent (here, n-heptane), causing the asphaltenes to precipitate out. The remaining solution was then passed through a chromatographic column, where saturates were first eluted with n-heptane. Aromatics are extracted with a slightly polar solvent (hexane), and resins are eluted with a more polar solvent (toluene). The isolated fractions are then quantified, providing insights into the composition of the sample.

3.3.2 Elemental analysis

Further, for the determination of weight % of C, H, N, and S, elemental analyzer (PerkinElmer 2400, USA) was employed. The oxygen content is estimated using the difference formula.

3.3.3 Viscosity

Viscosity of sample was measured using a Discovery HR-3 hybrid rheometer (TA, USA) instrument. Viscosity was measured at 40 °C (raised from 25 °C at a rate of 5 °C/min) under a constant shear rate of 10 s⁻¹. A peak hold phase followed, with measurements taken at 40 °C for a duration of 10 minutes, including a 3-minute soaking period. The sampling interval was set to 10 seconds per point. After the analysis, the instrument was cooled down to 25 °C.

3.3.4 Density

The density of the raw HVGO was determined manually by calculating the mass-to-volume ratio. A piece of parafilm, measuring 50 × 50 × 0.12 mm, was used to wrap an unknown amount of HVGO, which was then fully submerged in a 25 ml glass cylinder containing water initially filled to the 10 ml mark. Approximately 8 ml of water was displaced. The mass of the HVGO before and after wrapping in the parafilm was measured using a digital scale, and the values were recorded in grams.

3.3.5 Softening point

To measure the softening point the samples, about 15-20 g of pre-heated material was filled in a metallic ring and allowed to cool down in a refrigerator for about -5°C°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 glyceri, 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.

3.3.6 Thermogravimetric analysis

Thermogravimetric analysis was performed to evaluate thermal stability and to understand the extent of cross-linking which led to a high molecular weight heavy (addition) product. Approximately 10 g of selected samples was examined in an SDT Q600 V20.9 Build 20 thermogravimetric analyzer (TGA) coupled with a Differential Scanning Calorimeter (DSC). An alumina pan was used for both the reference and the samples. A nitrogen flow rate of 50 mL/min was maintained during the analysis and temperature was programmed from 30 to 950 °C with a ramp setting of 10 °C/min.

3.3.7 Boiling point analysis

Analysis was conducted on the samples using a SimDis system (Agilent) with Compass CDS software and Eclipse SIMDIST, following the ASTM D2887 SimDis-2 method. Helium served as the carrier gas, maintained at a flow rate of 20 ml/min. The equipment featured a DB-1 column measuring 10 m × 530 µm × 2.65 µm. The oven was programmed to heat from 0 °C to 600 °C, increasing at a rate of 20 °C/min. Around 1 gram of each sample (or product) was fully dissolved in approximately 4.5 mL of carbon disulfide (CS₂) and transferred into 5 mL vials. The injection volume used was 0.1 µL.

3.3.8 SEM analysis

The surface morphology of carbon fibers was evaluated by a scanning electron microscope (Quattro S FESEM, Massachusetts, USA) at an accelerating voltage from 200 to 30 kV, an Dispersive X-ray (EDX) detector for X-ray signals, and a low vacuum detector (LVD) for low vacuum SE signals. Beam deceleration with stage bias was -4000 V to +50 V.

3.3.9 Attenuated Total Reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) analysis

About 1 gram of each sample was placed in a 4 ml glass-vial. A drop from each sample was tested independently using a Nicolet iS50 FT-IR analyzer. The analysis was performed in Absorption mode.

CHAPTER 4

RESULTS AND DISCUSSION: CARBON FIBER FROM HEAVY VACUUM GAS OIL (HVGO)

This chapter examines the methods used to convert Heavy Vacuum Gas Oil (HVGO) into carbon fiber precursors. Asphaltenes were synthesized by controlling oxygen levels through two techniques: bubbling with mixing and blowing without mixing. These processes were conducted under varying temperatures, reaction times, and tetralin concentrations. The resulting samples were analyzed for key properties such as softening point and thermal stability to evaluate their suitability for carbon fiber production. The findings highlight how optimized methods can transform low-value HVGO into high-quality precursors, making them suitable for industrial applications in carbon fiber manufacturing.

4.1. Results: The Role Naphthenic-Aromatic Hydrocarbon

The autoxidation as a pretreatment process in the production of carbon fiber precursors from heavy oils, governed by a free radical mechanism, is highly dependent on the availability and transfer of oxygen, which is crucial for controlling the reaction kinetics, conversion rates, and product selectivity. As naphthenic-aromatic hydrocarbons would form comparatively stable free radicals, it would play a significant role in influencing the reaction outcomes, particularly under varying oxygen addition methods. This study investigated the effects of naphthenic-aromatic hydrocarbons on HVGO autoxidation

under two distinct oxygen introducing techniques: (i) bubbling with mixing and (ii) blowing without mixing, across different oxidation conditions. Both methods led to noticeable changes in key properties of HVGO, including asphaltenes content, viscosity, volatility, the formation of heavy products, softening point, and boiling point distribution.

4.1.1. Enhancement of Asphaltenes Content

Asphaltenes is the most complex portion of the petroleum fraction and mainly consists of high molecular weight hydrocarbons, and they are typically found in the heaviest portions of crude oils. These compounds are characterized by their solubility properties: asphaltenes are insoluble in light alkanes, such as *n*-heptane or pentane, but are soluble in aromatic solvents like toluene. The study investigated the changes in asphaltenes content in HVGO under different oxidation conditions, focusing on two temperatures (160 °C and 190 °C) and using two air introducing methods namely bubbling with mixing and blowing without mixing. The data presented in **Table 7** and **Figures 17 (a)** and **17 (b)** provide key insights into how these factors influence asphaltenes formation.

Table 7. A summary of the change in asphaltenes content, viscosity, and softening point during HVGO autoxidation in the presence of tetralin at different operating conditions.

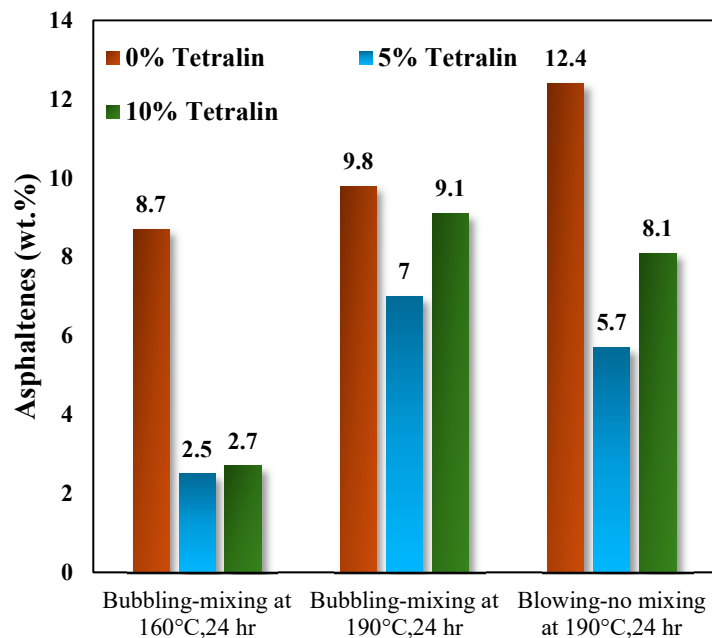
Air addition method	Ex. ID	Tetralin concentration %w/w	Time (h)	Temperature (°C)	Asphaltenes content (wt.%) _a	Viscosity at 25 °C (Pa.s) _b	Softening point (°C) ^a
Bubbling with mixing	A	0	24	160	8.7	4.77 ± 0.20	-
	B	0	24	190	9.8	6.49 ± 0.31	-
	C	5	24	160	2.5	4.66 ± 0.27	-
	D	5	24	190	7	5.57 ± 0.28	-
	E	10	24	160	2.7	1.98 ± 0.12	-
	F	10	24	190	9.1	4.39 ± 0.22	-
	G	20	24	160	4.2	1.2 ± 0.05	-
	H	20	24	190	8.7	1.48 ± 0.07	-
	I	30	24	160	3.6	0.40 ± 0.01	-
	J	30	24	190	14.7	0.68 ± 0.02	-
	K	0	48	190	15.9	19.9 ± 1.3	52.2
	L	5	48	190	17.9	23.15 ± 1.4	58.6
Blowing without mixing	M	0	24	160	1.5	3.13 ± 0.16	-
	N	0	24	190	12.4	10.8 ± 0.63	-
	O	5	24	160	2.4	2.73 ± 0.15	-
	P	5	24	190	5.7	3.69 ± 0.28	48.3
	Q	10	24	160	1.6	1.03 ± 0.04	-
	R	10	24	190	8.1	3.25 ± 0.17	-
	S	0	48	190	17.1	26.7 ± 1.9	57.6
	T	5	48	190	32.8	51.5 ± 8.9	145
	U	0	72	190	39.8	80.8 ± 20.6	165
	V	5	72	190	47.2	117.6 ± 58	210

^aAnalysis performed in duplicated, values reported as average.

^bAnalysis performed in duplicated, values reported as average ± one sample standard deviation.

As shown in **Table 7**, the asphaltenes content in the experiments varied significantly based on the air addition method, tetralin concentration, and temperature. For the experiments using air bubbling with mixing, the asphaltenes content ranged from 2.5 wt.% to 14.7 wt.%, with higher temperatures (190 °C) generally yielding more asphaltenes, particularly when tetralin concentrations were increased to 30 wt.% (Experiment J). In contrast, experiments

with air blowing without mixing showed a broader range of asphaltenes content, with a notable increase at longer reaction times and higher temperatures. The highest asphaltenes content, 24.1 wt. %, was observed in Experiment V (72 hours, 5% tetralin, 190 °C), highlighting the impact of extended oxidation times and limited oxygen availability.



[a]

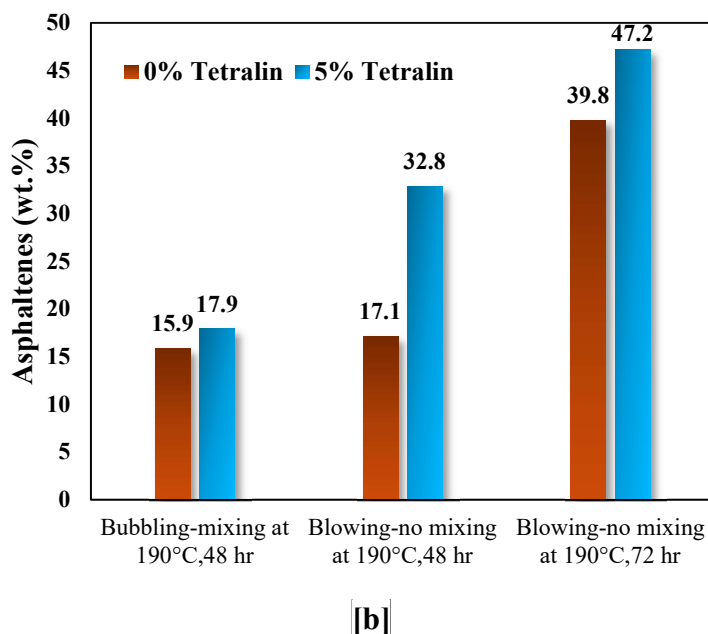


Figure 17. The change in asphaltenes content during HVGO autoxidation in the presence of tetralin and different air introducing method [a]: at 160 - 190 °C for 24 h, [b] at 190 °C for 48 - 72 h.

In **Figure 17 (a)**, the change in asphaltenes content is plotted against tetralin concentration under both bubbling air with mixing and blowing air without mixing conditions. At 160 °C, the asphaltenes content decreased as tetralin concentration increased in the bubbling air with mixing method. For instance, in the absence of tetralin, the asphaltenes content was 8.7 wt.%, which dropped to 2.7 wt.% at 10 % tetralin. In contrast, the blowing air without mixing at 160 °C for 24 h resulted in an initial asphaltene content of 1.5 wt. %, which remained relatively low even with increased tetralin concentrations. At 190 °C, the behavior shifted. For bubbling air with mixing, the asphaltene content initially decreased to 2.5 wt. % at 5 % tetralin but raised sharply to 14.7 wt.% at 30 % tetralin. Meanwhile, blowing air without mixing at 190°C shows higher asphaltene contents throughout. The maximum value of 12.4 wt. % was achieved without tetralin, decreasing slightly as tetralin concentration increased. **Figure 17 (b)** emphasizes the impact of prolonged oxidation times

and higher temperatures under the blowing without mixing method. At 48 hours, the asphaltenes content varies notably depending on the air addition method and tetralin concentration. Under the blowing without mixing method at 190°C, the asphaltenes content is 17.1 wt.% with 0% tetralin, as shown in Table 2. When 5 wt. % tetralin was introduced, the asphaltenes content increased to 32.8 wt. %. In contrast, under bubbling with mixing conditions at the same temperature and duration, the asphaltenes content remained comparatively lower at 15.9 wt. % and 17.9 wt. %, respectively, even with similar tetralin concentrations. As the reaction time extended to 72 hours, the situation became more pronounced. Under the blowing without mixing method, the asphaltenes content escalated dramatically to 47.2 wt. % with 5 % tetralin, compared to 39.8 wt. % with 0 % tetralin at identical condition of blowing without mixing at 190 °C.

In summary, the highest asphaltenes content (47.2 wt. %) is observed with 5 % tetralin at 72 hours and 190 °C using the blowing air without mixing method, while the lowest content (1.5 wt. %) occurs at 160 °C with no tetralin and the same air addition method.

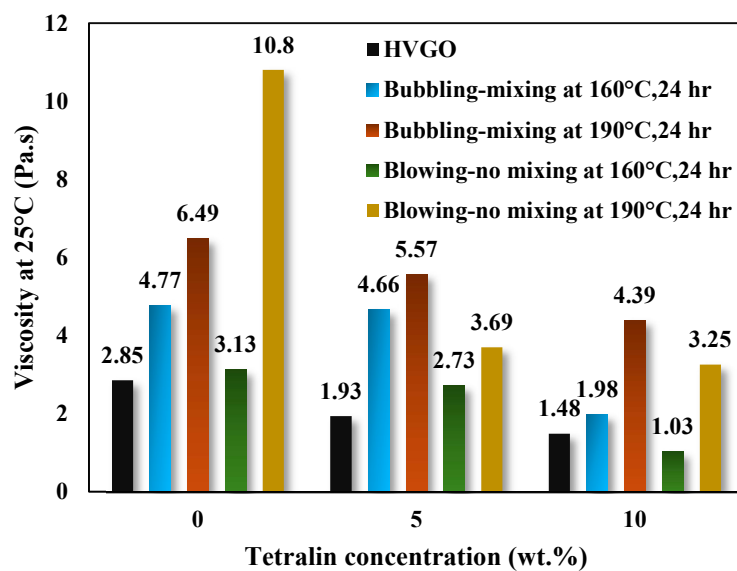
4.1.2. Viscosity

Viscosity is one of the most important physical properties that would change during the autoxidation of heavy vacuum gas oil (HVGO). **Figures 18 (a) and 18 (b)** illustrate the impact of different oxygen addition methods and tetralin concentrations on the viscosity of HVGO during autoxidation at two temperatures, 160 °C and 190 °C. These figures, along with specific data points from **Table 8**, reveal significant trends and values that highlight how temperature, mixing, and tetralin concentration influence the viscosity of HVGO.

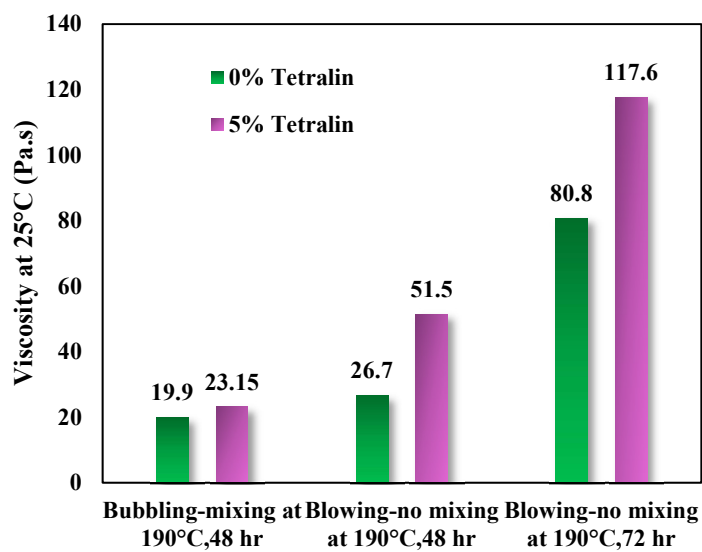
At 160 °C, **Figure 18(a)** shows that under the bubbling with mixing method, viscosity values remain relatively low compared to other methods. For instance, viscosity started at 4.77 Pa.s at 0 % tetralin and dropped significantly to 1.93 Pa.s at 10 % tetralin. Similarly, under the blowing without mixing method at 160°C, viscosity increased slightly with tetralin concentration, starting from 3.13 Pa.s at 0 wt. % tetralin (Experiment M) and reaching 1.03 Pa.s at 10% tetralin.

Table 8. A summary of the change in viscosity, during HVGO autoxidation in the presence of tetralin at different operating conditions.

Air addition method	Ex. ID	Tetralin concentration %w/w	Time (h)	Temperature (°C)	Viscosity at 25 °C (Pa.s)
Bubbling with mixing	A	0	24	160	4.77 ± 0.20
	B	0	24	190	6.49 ± 0.31
	C	5	24	160	4.66 ± 0.27
	D	5	24	190	5.57 ± 0.28
	E	10	24	160	1.98 ± 0.12
	F	10	24	190	4.39 ± 0.22
	G	20	24	160	1.2 ± 0.05
	H	20	24	190	1.48 ± 0.07
	I	30	24	160	0.40 ± 0.01
	J	30	24	190	0.68 ± 0.02
	K	0	48	190	19.9 ± 1.3
	L	5	48	190	23.15 ± 1.4
Blowing without mixing	M	0	24	160	3.13 ± 0.16
	N	0	24	190	10.8 ± 0.63
	O	5	24	160	2.73 ± 0.15
	P	5	24	190	3.69 ± 0.28
	Q	10	24	160	1.03 ± 0.04
	R	10	24	190	3.25 ± 0.17
	S	0	48	190	26.7 ± 1.9
	T	5	48	190	51.5 ± 8.9
	U	0	72	190	80.8 ± 20.6



[a]



[b]

Figure 18. Viscosity changes, at 24 hours oxidation time [a], at longer oxidation time and 190°C [b].

At 190°C, the situation became more intricate, as illustrated in **Figure 18 (a)**. Using the bubbling with mixing technique, the viscosity trends remained consistent. For instance, the viscosity began at 6.49 Pa.s with 0% tetralin and dropped to 4.39 Pa.s at 10% tetralin, with Table 2 showing an even further reduction to 0.68 Pa.s at 30% tetralin. However, when using the blowing without mixing method at the same temperature, the viscosity at 0% tetralin rose significantly, reaching 10.8 Pa.s. The other viscosity values with tetralin, though, followed a similar pattern to those observed at 160°C.

Figure 18 (b) further explores the effect of prolonged oxidation times at 190°C under the blowing without mixing method. The bar graph shows a significant increase in viscosity over time. After 48 hours, viscosity reaches 51.5 Pa.s at 0 % tetralin and 26.7 Pa.s at 5% tetralin, where under the bubbling with mixing method for 48 hours, the viscosity values are much lower, 19.9 Pa.s at 0% tetralin and 23.15 Pa.s at 5% tetralin. However, after 72 hours, viscosity increases dramatically to 117.6 Pa.s at 5 % tetralin, compared to 80.8 Pa.s at 0 % tetralin.

In the experiments, the highest reported viscosities occurred under the blowing without mixing method at 190°C. Notably, after 72 hours, the viscosity reached 117.6 Pa.s with 5 % tetralin, and 80.8 Pa.s with 0 % tetralin. Additionally, after 48 hours, viscosity was 51.5 Pa.s with 5 % tetralin and 26.7 Pa.s with 0 % tetralin. These values demonstrate the substantial impact of prolonged oxidation and the absence of mixing on the viscosity of HVGO.

4.1.3. Softening Point

The softening point is a key indicator of the thermal properties of oxidized heavy vacuum gas oil (HVGO), reflecting the extent of oxidation and the formation of heavier products.

The softening point of raw HVGO is 37°C (**Table 6**), which serves as a baseline for comparison with the values observed under different oxidation conditions in **Table 7**.

At 190°C (48 hours), when examining the bubbling with mixing method at 190 °C for 48 hours, the softening point showed a moderate increase compared to the raw HVGO. Specifically, the softening point reached to 52.2 °C at 0 wt. % tetralin (Experiment K) and slightly risen to 58.6 °C at 5 wt% tetralin (Experiment L). In contrast, the blowing without mixing method at 190 °C resulted in a more significant increase in the softening point when comparing 24 hours and 48 hours. After 48 hours, the softening point was 57.6°C at 0 wt. % tetralin (Experiment S). When 5% tetralin was used under the blowing without mixing method at 190 °C for 48 hours, the softening point escalated dramatically to 145 °C (Experiment T). The effects of prolonged oxidation times under the blowing without mixing method became even more extreme at 190°C. After 72 hours, the softening point increases drastically to 165°C at 0 % tetralin (Experiment U) and reached an extraordinarily high 210 °C at 5 wt. % tetralin (Experiment V).

4.1.4. Extent of Heavy Products Formation

The thermogravimetric analysis (TGA) results in **Figure 19** demonstrate the thermal stability of heavy vacuum gas oil (HVGO) and its oxidation products under various

experimental conditions. Raw HVGO shows the least thermal stability, with early weight loss indicating the presence of lighter, more volatile components. This is evident from the sharp decrease in weight, reflecting a rapid decomposition. When HVGO is oxidized using the blowing without mixing method at 190°C for 48 hours with 5% tetralin (Experiment T), there is a noticeable improvement in thermal stability. The delayed onset of decomposition and the fact that 7.9% of the material remains suggests the formation of heavier, more stable oxidation products compared to raw HVGO, which nearly fully decomposes at lower temperatures. Further oxidation at 190°C for 72 hours, both without tetralin (Experiment U) and with tetralin (Experiment V), leads to even greater thermal stability. Prolonged oxidation time allows for a more complete transformation of HVGO into heavier and more thermally stable compounds, reducing the proportion of volatile components.

The highest thermal stability is observed in the asphaltenes extracted from the HVGO + 5% tetralin sample (Experiment V) after 72 hours. These asphaltenes, separated using solvent extraction with n-heptane as described in chapter 3, exhibit the greatest resistance to thermal decomposition. This reflects the formation of a highly stable asphaltene fraction, which decomposes at much higher temperatures, highlighting the effect of both tetralin and extended oxidation time in enhancing thermal stability. This explanation effectively integrates the experimental findings and the role of tetralin and oxidation time in improving the thermal stability of HVGO.

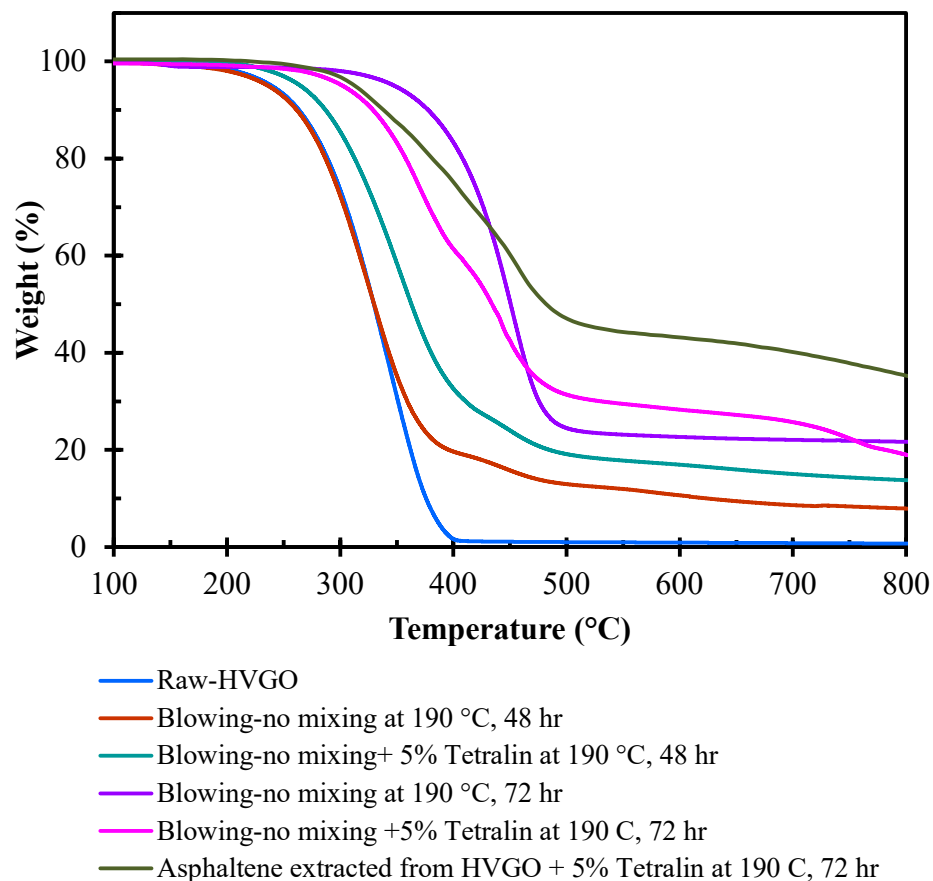


Figure 19. TGA thermograms for raw- and oxidized-HVGO at different operating conditions.

4.1.5. Changes in Volatility

The SIMDIS analysis (**Figure 20**) provides a clear indication how autoxidation maintaining different conditions changed the boiling points of the HVGO. It also correlates with the thermal stability results from TGA for the different samples. In **Figure 20**, Raw-HVGO showed a sharp rise in recovery percentage at temperature around 80 °C and after 400 °C, indicating a significant portion of lighter, volatile components. This aligns with the

TGA (**Figure 19**), where Raw-HVGO exhibited early thermal decomposition due to its lower boiling point fractions.

In contrast, the sample treated with blowing and 5% Tetralin at 190°C for 72 hours (Experiment V) shows a broader, more gradual recovery curve, covering a wider range of boiling points (300°C to 600°C). The recovery starts earlier than in Raw-HVGO, indicating that this sample has some lighter components, like unreacted tetralin. The recovery percentage increases steadily from 30% to 90%, spread over a wider temperature range (around 200°C to 600°C), suggesting the presence of both lighter and heavier fractions.

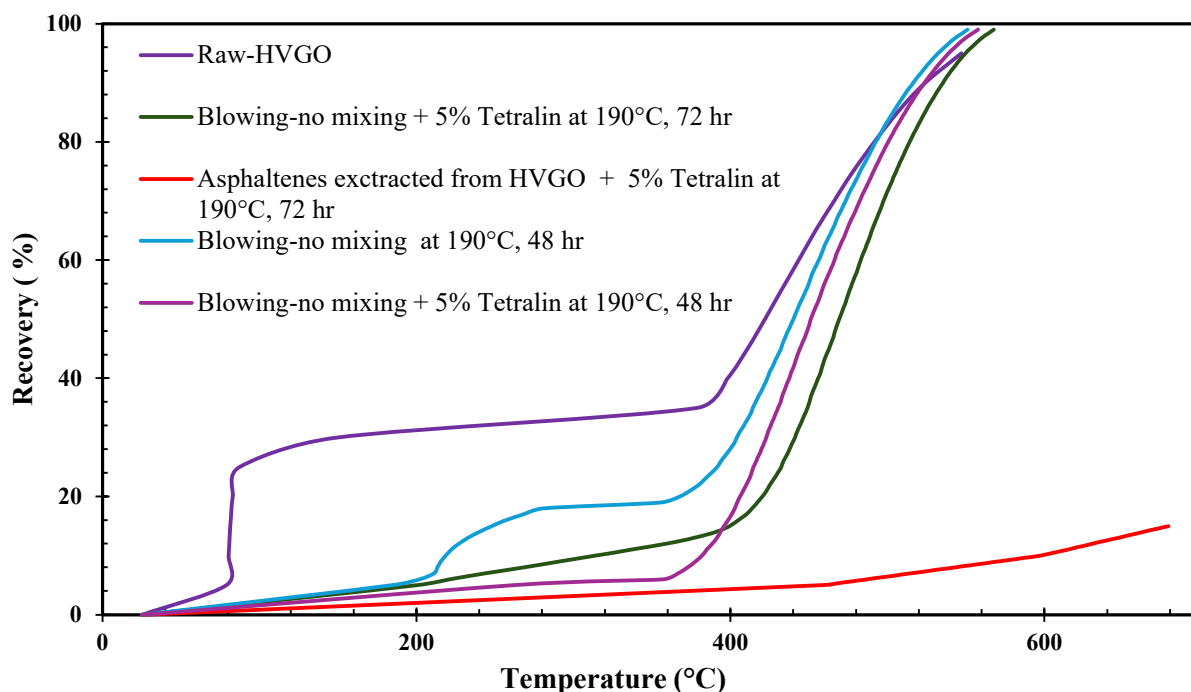


Figure 20. Boiling point distribution of HVGO, Blowing-no mixing + 5% Tetralin at 190°C, 72 hr and its asphaltene.

The asphaltene extracted from HVGO exhibits the highest thermal stability, as seen in **Figure 20**, where recovery begins much later, around 400°C, and rises very gradually. This

indicates that asphaltenes have significantly higher boiling points than the other samples and take much longer to evaporate. This mirrors the TGA results (**Figure 19**), which indicated the resistance of asphaltenes to decomposition, further confirming their high boiling points and stability.

4.1.6. Change in Elemental Composition and Functional groups

Elemental and FTIR analyses are essential tools for understanding the chemical changes in HVGO during oxidation. **Table 8** presents the elemental composition of raw HVGO and its oxidation products under various conditions. Raw HVGO exhibited a high carbon content (85.3 %) and significant hydrogen content (11.9 %), resulting in an H/C ratio of 1.66, which indicated a predominant aliphatic and aromatic structures. As oxidation progresses, particularly in Experiment T (blowing without mixing + 5% tetralin at 190°C for 48 hours), the H/C ratio decreased to 1.34, indicating a shift towards more aromatic compounds. Simultaneously, the oxygen content rises to 3.15 %, indicating that oxidation had incorporated more oxygen into the molecular structure. This trend continued in Experiment U (blowing without mixing at 190°C for 72 hours), where the oxygen content increased further to 3.8 %, and in Experiment V (blowing without mixing + 5% tetralin at 190°C for 72 hours), where it reached 3.41%, reflecting the formation of higher oxygen containing products. The asphaltenes, with the lowest H/C ratio of 0.95 and oxygen content of 1.2 %, represent the most condensed and aromatic structure, demonstrating extensive oxidation and a presence of oxygenated species.

Table 9. Elemental composition (wt.%) HVGO and oxidized HVGOs

Samples	ID	C	H	S	N	O	H/C
HVGO	-	85.3	11.9	2.3	0.1	0.4	1.6
Blowing-no mixing + 5% Tetralin at 190°C, 48 hr	T	82.2	9.25	4.2	1.1	3.1	1.3
Blowing-no mixing at 190°C, 72 hr	U	81.6	9.22	4.2	1.1	3.8	1.3
Blowing-no mixing + 5% Tetralin at 190°C, 72 hr	V	82.5	8.84	4.2	1.0	3.4	1.3
Asphaltenes derived from oxidized HVGO + 5% Tetralin at 190°C, 72 hr	-	86.8	6.95	4.3	0.7	1.2	0.95

Figure 21 presents the FTIR spectra of Raw-HVGO, various treated HVGO samples, and asphaltenes extracted from HVGO + 5% Tetralin at 190°C for 72 hours. The spectra reveal key differences in the chemical composition of the samples, with specific attention paid to the absorption bands related to aromatic (C=C) and aliphatic (C-H) hydrocarbons. In the C=C aromatic region (1500-1600 cm^{-1}), the asphaltenes show a significantly broader and more intense absorption peak compared to the other samples, indicating a higher concentration of aromatic compounds. This broadened stretch suggests that the asphaltenes contain a more complex and densely packed network of polycyclic aromatic structures, characteristic of their high molecular weight and stability. In contrast, the other samples, including Raw-HVGO and the oxidized HVGO samples, exhibit narrower peaks in this region, reflecting the presence of fewer and less complex aromatic compounds. In the 2800-3000 cm^{-1} region, corresponding to the C-H stretch of aliphatic hydrocarbons, the asphaltenes display minimal absorption. This indicates that the asphaltenes contain a lower proportion of aliphatic hydrocarbons, which are more prevalent in Raw-HVGO and the treated HVGO samples. The stronger absorption in this region for Raw-HVGO and the oxidized samples suggests a higher concentration of aliphatic hydrocarbons, which are

reduced in the asphaltenes. The addition of tetralin during the oxidation process appears to slightly reduce the intensity of the aliphatic stretch in the treated samples, indicating a transformation toward more aromatic structures.

Overall, the FTIR spectra demonstrate that asphaltenes are predominantly composed of aromatic hydrocarbons, as indicated by the prominent C=C stretch and minimal aliphatic content.

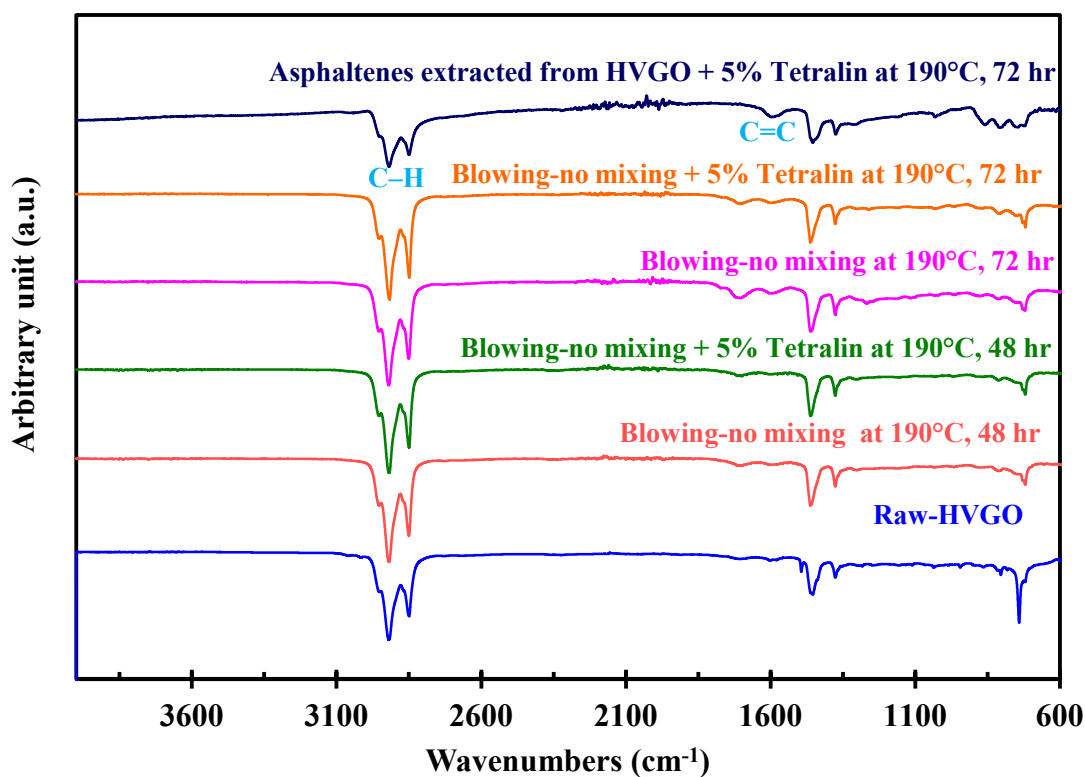


Figure 21. FTIR spectrum of HVGO, oxidized-HVGO, and its derived asphaltenes

These findings highlight the chemical differences between asphaltenes and the untreated or partially oxidized HVGO samples, with the former being more thermally stable due to their aromatic-rich composition. This analysis aligns with previous observations regarding

the thermal behavior of asphaltenes and the impact of oxidation and Tetralin treatment on HVGO composition

4.2. Discussion

4.2.1 Autoxidation Chemistry Underlying Changes in Material Properties

Autoxidation is a controlled (mild) thermo-chemical process where hydrocarbons react with molecular oxygen at relatively low temperatures. Unlike combustion, autoxidation occurs under conditions that allow for a slower, controlled oxidation process, preventing the rapid, exothermic reactions characteristic of burning. This controlled environment is crucial for understanding the transformation of HVGO components, under the experimental conditions applied. The reaction network of aliphatic hydrocarbon autoxidation, as illustrated in **Figure 12**, outline the key steps involved in this oxidation process. Initially, aliphatic hydrocarbons react with oxygen to form highly reactive hydrocarbon free radicals. These radicals can either combine with other hydrocarbons to produce addition (heavy) products when oxygen is limited (Step II), or continue to react with excess oxygen (Step III), leading to the formation of hydroperoxides. Hydroperoxides are unstable intermediates that can decompose into alcohols (Step IV) or undergo further oxidation to produce carbonyl compounds (Step V), such as aldehydes and ketones. Alcohols that form can also be further oxidized to produce ketones. In the context of HVGO autoxidation, cyclic saturated hydrocarbons, and naphthenic-aromatic hydrocarbons, are the primary components susceptible to autoxidation. Linear and branched hydrocarbons,

as well as non-naphthenic aromatics, are less reactive under these conditions due to their more stable structures and stronger C-H bonds. Therefore, the autoxidation process primarily affects the cyclic saturated and naphthenic aromatic hydrocarbons in HVGO

The production of free radicals during autoxidation is highly temperature dependent. As temperature increases, the rate of free radical formation accelerates, enhancing the likelihood of forming addition products, as shown in **Figure 22** at the oxygen limited conditions. This mechanism aligned with the observed increased in asphaltenes content and viscosity under higher temperatures and extended oxidation times, as depicted in **Figures 17 (a) and 18 (a)**, respectively. The prolonged oxidation time further exacerbated free radical production, leading to the formation of heavier compounds, which were reflected in the increased asphaltenes content (**Figure 17 (b)**), higher viscosity (**Figure 18 (b)**), elevated softening points (**Table 7**), and greater thermal stability (**Figure 19**). (Siddiquee & De Klerk, 2014a)

Building on the understanding that autoxidation can significantly enhance the asphaltenes content of HVGO and subsequently improve its physical properties, it is important to consider the role of air addition methods, specifically air bubbling with mixing and air blowing without mixing. These methods influence the efficiency of the oxidation process, even when the reaction temperature is held constant.

Autoxidation inherently increases the asphaltenes content, as discussed previously, but the method of air introduction can further modulate this effect. In the air bubbling with mixing method, oxygen is assumed to be evenly distributed throughout the medium due to effective mixing. This uniform distribution allows for a consistent and controlled oxidation

process across the entire HVGO mass. In contrast, air blowing without mixing introduces oxygen only at the interface between the air and HVGO. The lack of mixing means that some oxygen may not fully interact with the HVGO, leading to a lower overall oxygen availability compared to air bubbling. However, this limited and controlled oxygen exposure during air blowing enhances the likelihood of the oxidation process following step II in **Figure 4-6** (formation of addition products). As HVGO molecules at the interface generate free radicals, the consistent, yet limited, availability of oxygen allows for the stepwise addition of heavier molecules. These heavier molecules then settle by gravity, allowing lighter molecules to replace them and undergo the same process, leading to the formation of heavy products in a more ordered and consistent manner. In contrast, air bubbling with mixing introduces more oxygen to the HVGO molecules, increasing the likelihood of the oxidation process following step III in **Figure 22**, which resulted in the formation of hydroperoxides, and potentially less controlled heavy product formation compared to air blowing.

For instance, as shown in **Table 7**, Experiment N (air blowing without mixing, 24 hours, 190°C) resulted in a higher asphaltenes content of 12.4% compared to Experiment B (air bubbling with mixing, 24 hours, 190°C), which had an asphaltenes content of 9.8 %. This higher asphaltenes content in Experiment N suggests that the controlled and gradual oxidation process enabled by air blowing without mixing is more effective in forming heavy products. However, at lower temperatures (160 °C), the results shift. Experiment A (air bubbling with mixing, 24 hours, 160°C) resulted in a higher asphaltenes content of 8.7% compared to Experiment M (air blowing without mixing, 24 hours, 160°C), which had an asphaltenes content of 1.5%. This difference might be due to the formation of lower

free radical at the interface during air blowing without mixing at the lower temperature, leading to a reduced rate of heavy product formation. The limited interaction of oxygen with HVGO molecules inside the reactor bulk restricts oxidation, resulting in less asphaltene formation. In contrast, air bubbling with mixing ensures that oxygen interacts with the molecules throughout the reactor, allowing oxidation to occur, albeit at a lower rate than at 190 °C.

These observations highlight the importance of the air addition method in influencing the autoxidation process, particularly how it impacts the distribution and availability of oxygen, which in turn affects asphaltene formation and the overall physical properties of HVGO. The role of tetralin in modifying these effects under similar conditions will be discussed next.

Tetralin, a naphthenic aromatic hydrocarbon, plays a significant role in the autoxidation process of HVGO, as it is one of the molecules within HVGO that is particularly susceptible to oxidation. Tetralin oxidation itself at different operating conditions lead to form dark-heavy products which were confirmed in our previous study that resulted the increased in viscosity, and density. (Muhammad Nurunnabi Siddiquee, 2014; Siddiquee & De Klerk, 2014) As illustrated in **Figure 23**, the oxidation of tetralin would depends heavily on the availability of oxygen. (Muhammad Nurunnabi Siddiquee, 2014; Siddiquee, De Klerk, et al., 2016; Siddiquee & De Klerk, 2014) When oxygen levels are high, tetralin tends to form products such as alcohols and ketones. However, under controlled, limited oxygen conditions, tetralin primarily forms addition products, which are generally more desirable for enhancing the properties of HVGO as illustrated in **Figure 24**.

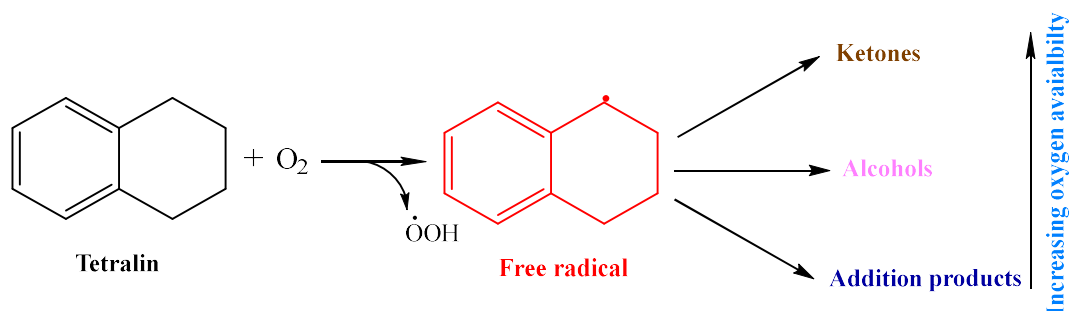


Figure 22. A typical reaction pathway during tetralin oxidation (Siddiquee et al., 2022).

Tetralin's (A) hydrogen at the α -position is susceptible to hydrogen abstraction, leading to the formation of a free radical (B). In oxygen-limited conditions, this free radical is more likely to participate in addition reactions within the HVGO matrix. However, in higher oxygen environments, the free radicals can react with molecular oxygen to form peroxy radicals. These oxygen-containing radicals may result in the production of oxygenates like alcohols or ketones, as indicated in **Figure 24**.

After hydrogen abstraction (Step II), the tetralin molecule can convert into an olefin (C) through hydrogen disproportionation. (Siddiquee, De Klerk, et al., 2016) This olefin is reactive and can combine with free radicals already present in the HVGO, such as those forming from more complex structures (H) and /or (I). The olefin (C) can also combine to form typical dimerized product (D), which have been confirmed through GC-MS analysis of products like tetralin indene and indane in previous studies (Muhammad Nurunnabi Siddiquee, 2014b; Siddiquee & De Klerk, 2014).

The dimerized products can undergo further reactions with HVGO free radicals, leading to the formation of even more complex and heavier products (F or G). This progression would lead to a significant increase in molecular weight and, consequently, heavier polynuclear

aromatic structures. Additionally, these free radicals might interact with heteroatoms present in HVGO, possibly contributing to further chemical transformations.(Siddiquee & De Klerk, 2014a; Siddiquee & Klerk, 2015)

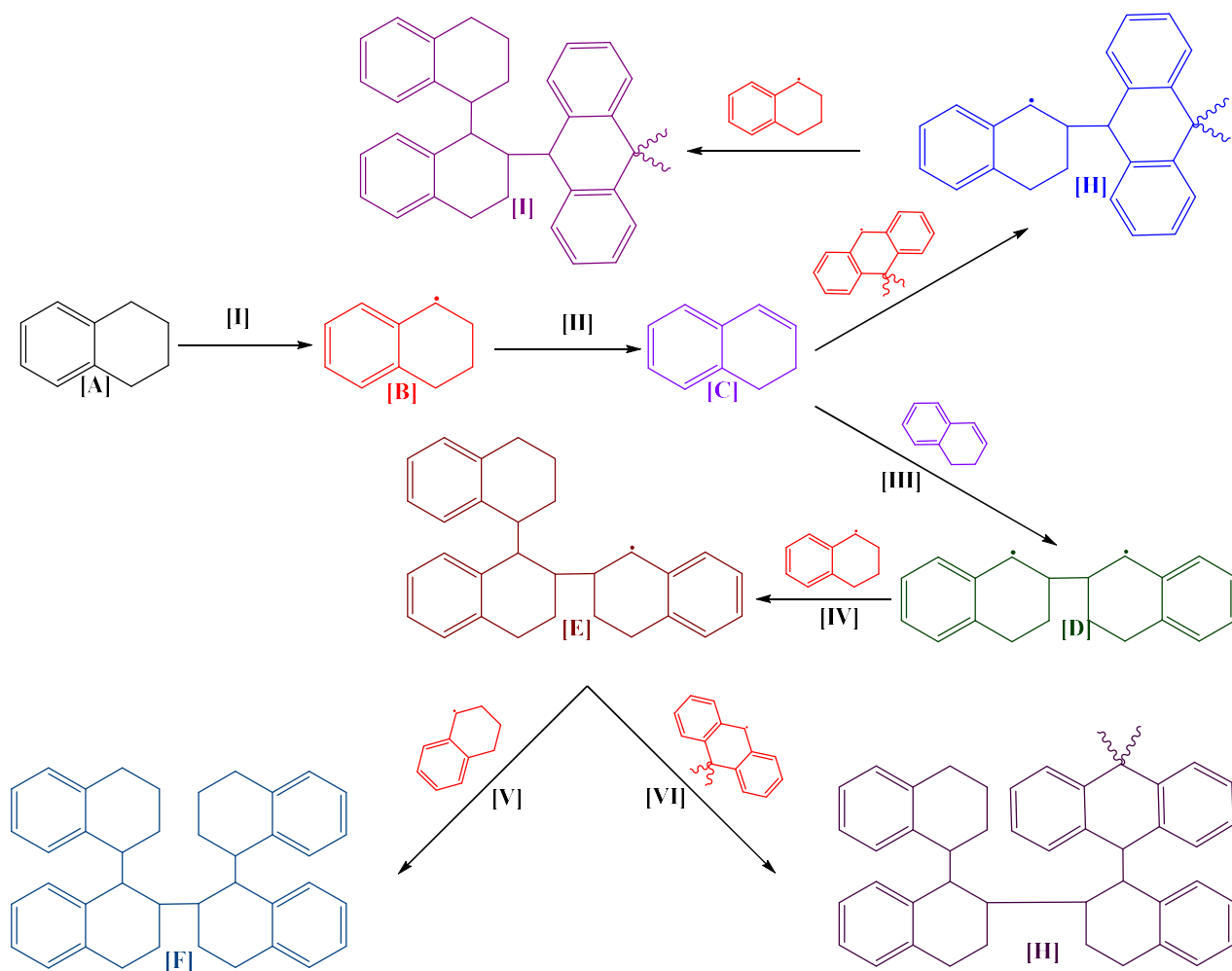


Figure 23. Typical potential addition reaction during the autooxidation of HVGO in the presence of naphthenic aromatic hydrocarbon at the low oxygen availability.

The experimental results directly reflect the theoretical role of tetralin as outlined in your explanation. For example; In experiment V (5% tetralin at 190 °C for 72 hours with air blowing without mixing), the asphaltenes content reached 47.2 wt. %, with viscosity

increased to 117.6 Pa.s, and softening point of 210 °C compared to 39.8 wt. % asphaltenes, 80.8 Pa.s viscosity, and 165°C for experiment U. These results align with tetralin's role in promoting reactions that enhance the material's resistance to thermal degradation, making the oxidized HVGO more suitable for high-temperature applications such as carbon fiber production.

4.2.2 Suitability of Oxidized HVGO as Carbon Fiber Precursors

The suitability of asphaltenes extracted from oxidized HVGO with tetralin as a carbon fiber precursor can be critically assessed by comparing its properties with literature values (Table 10). The softening point of the asphaltenes-based precursor in this study is 197°C, which aligns well with the reported literature range of 180°C to 239°C. This higher softening point suggests good thermal processing potential, which is vital for melt spinning and stabilization steps. It also implies better thermal resistance, a critical factor during oxidative stabilization and carbonization.

Table 10. Suitability of produced carbon fiber precursor.

Property	Current study	Literature	References
Softening Point	- 197 °C ^a	- 239 °C - 180 °C	(Li et al., 2018; Saad et al., 2022)
Thermal Stability	- 800 °C	- +950 °C	(Islam et al., 2024)
H/C	- 1.04	- 1.14 - 1.26	(Y. Kim et al., 2021b; Saad et al., 2022)
Green Fiber Diameter	- 70 µm	- 18.1 µm - 20.3 µm	(Y. Kim et al., 2021b)

^ameasured

The suitability of a material as a carbon fiber precursor is critically dependent on its ability to undergo melt-spinning, a process where the material is extruded through a spinneret to form fibers. This process requires the material to exhibit specific thermal and rheological properties to ensure continuous fiber formation without breaking or forming defects. The ability to produce green fiber is a key indicator of the material's suitability for carbon fiber production.

In **Table 11**, the melt-spinning ability of various samples is summarized, with key details such as temperature and spinning rate. Experiment T (blowing without mixing with 5% tetralin at 190°C for 48 hours) and Experiment V (blowing without mixing with 5% tetralin at 190 °C for 72 hours) could not produce green fibers, as only droplets formed at temperatures up to 210 °C and 240°C, respectively. Similarly, Experiment U (blowing without mixing at 190°C for 72 hours) also failed to produce fibers, with droplets forming up to 200 °C. In contrast, asphaltenes derived from oxidized HVGO was successfully melt-spun at 240 °C and a spinning rate of 400 rpm, yielding green fibers (**Figure 25**) with a 70 µm diameter. These observations highlight that only asphaltenes derived from oxidized HVGO was suitable for carbon fiber production under the tested condition

Table 11. A summary of melt-spinning conditions and resulted green fibers.

Sample	Spinning Temperature	Spinning rate (rpm)	Comments
Blowing-no mixing + 5% tetralin at 190°C, 48 hr	- ^a	- ^a	Only droplet came out from the spinneret at up to 210°C
Blowing-no mixing at 190°C, 72 hr	- ^a	- ^a	Only droplet came out from the spinneret at up to 200°C
Blowing-no mixing + 5% tetralin at 190°C, 72 hr	- ^a	- ^a	Only droplet came out from the spinneret at up to 240°C

Asphaltenes derived from oxidized 240°C HVGO + tetralin ^a not spinnable	400	Produce green fiber with 70 μ m diameter
--	-----	---

The failure of Experiment T (blowing without mixing, with 5% tetralin at 190°C for 48 hours), Experiment V (blowing without mixing, with 5% tetralin at 190°C for 72 hours), and Experiment U (blowing without mixing at 190°C for 72 hours) to form green fibers can be attributed to the presence of other major constituents, such as saturates, aromatics, and resins, in addition to asphaltenes. These lighter components lack the ability to undergo melt-spinning due to their lower molecular weights and weaker thermal stability compared to asphaltenes. Asphaltenes, which is heavier and more thermally stable, was better suited for the formation of continuous fibers during melt-spinning. The lighter compounds present in saturates, aromatics, and resins would be more volatile and would not exhibit the necessary rheological properties required for fiber formation, resulting in the formation of droplets rather than continuous filaments.

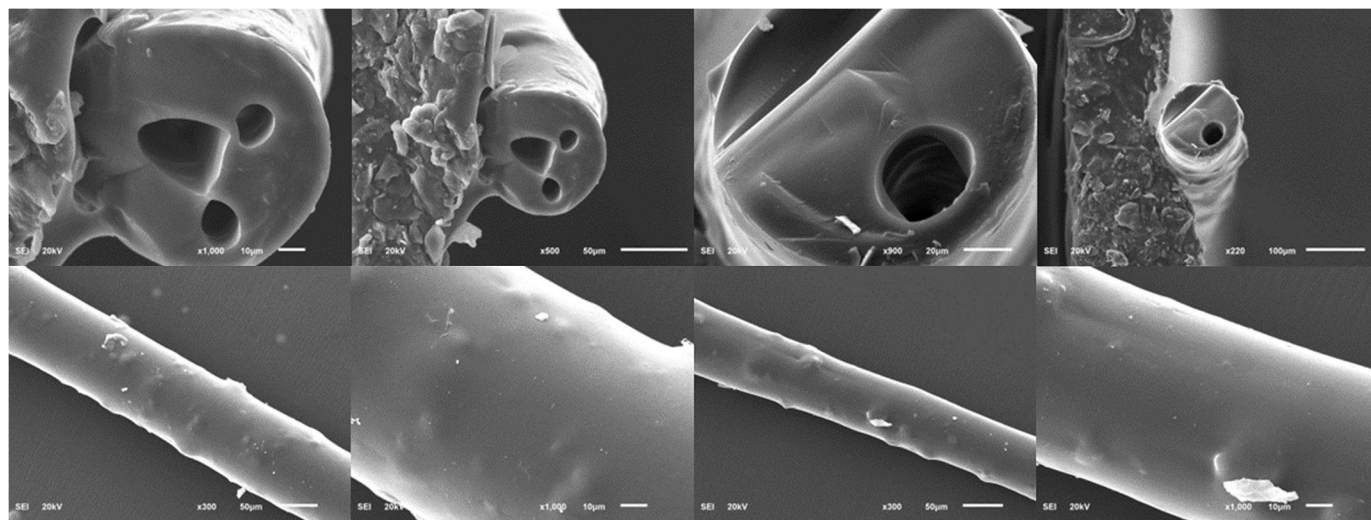


Figure 24. SEM picture of green fiber from autoxidized HVGO derived asphaltenes.]

Regarding thermal stability, the produced carbon fibers precursors were stable up to 800°C, slightly below the literature value of 950°C. While this is a notable difference, the achieved stability is sufficient for many applications. Process optimization, such as longer stabilization or higher carbonization temperatures, would enhance thermal resistance closer to the literature standard.

The H/C ratio of 0.95 in the current study is lower than the literature values (1.14 to 1.26), indicating a higher degree of aromatization, which is favorable as carbon fiber precursors. A lower H/C ratio suggests fewer volatiles and a higher carbon yield during carbonization, potentially improving the mechanical properties of the final carbon fibers. The green fiber diameter in this study (70 μm) exceeds the range reported in the literature (18.1 μm to 20.3 μm), likely due to the relatively low spinning speed (400 rpm).

The production of carbon fibers from asphaltenes, follows a systematic process designed to enhance both the physical and chemical properties of the material. Carbon fiber was produced from the asphaltenes derived from the autoxidized HVGO with 5 % tetralin (Experiment V) following stabilization and carbonization process described in chapter 3. The resulted carbon fibers had a reduced diameter of 40 - 50 μm , as depicted in **Figure 26**, and also have carbon content of 91.6 % with H/C is 0.106. Which is still larger than the literature range of 3.5 μm to 5 μm . This could be attributed to the relatively low carbonization temperature (800°C), which may have inhibited the complete removal of non-carbon elements.

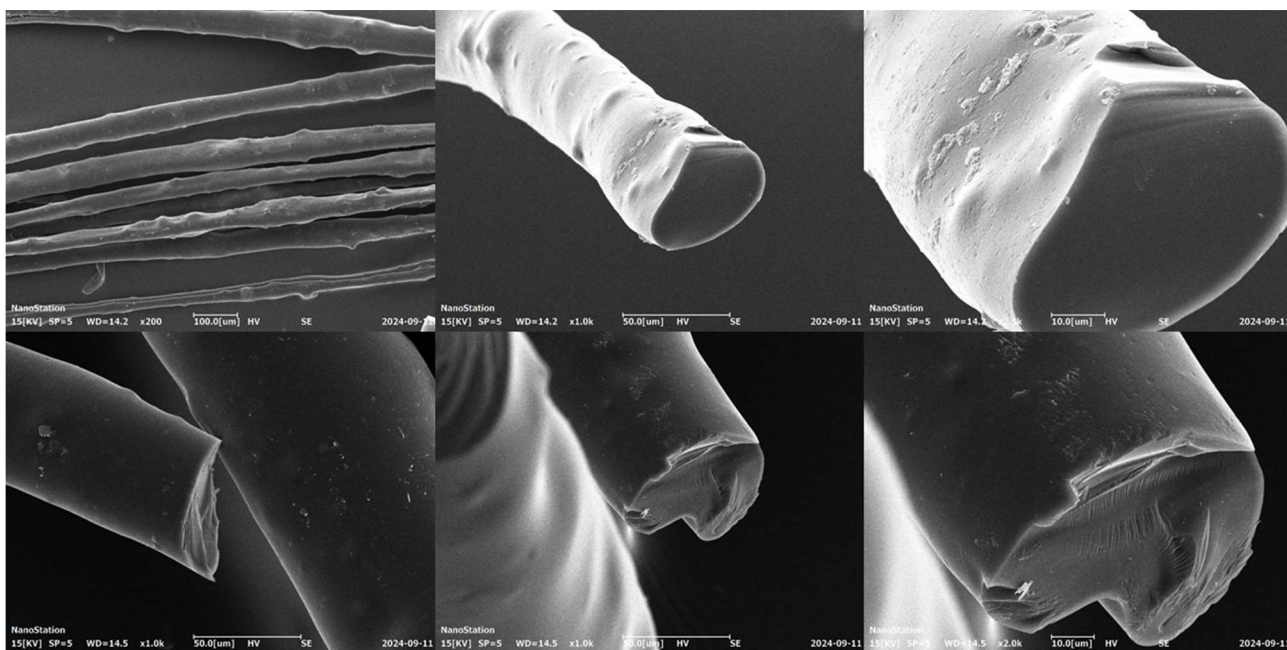


Figure 25. SEM picture of carbon fiber from Asphaltenes.

In order to check the **thermal stability** of resulted carbon fiber, TGA analysis was performed. From **Figure 27**, it is cleared that almost all the degradation of Raw-HVGO occurs mainly between 230 °C and 400 °C. In this temperature range, the steepest slope of curve indicating un-stabilized characteristic of Raw-HVGO. On the other hand, green fiber showed a widest thermal degradation range with lower inclination indicating an improvement in the thermal stability. Further, the horizontal line of the carbonized fiber indicating the insensitivity of the degradation for the temperature values meaning that the fiber had become thermally stabilized.

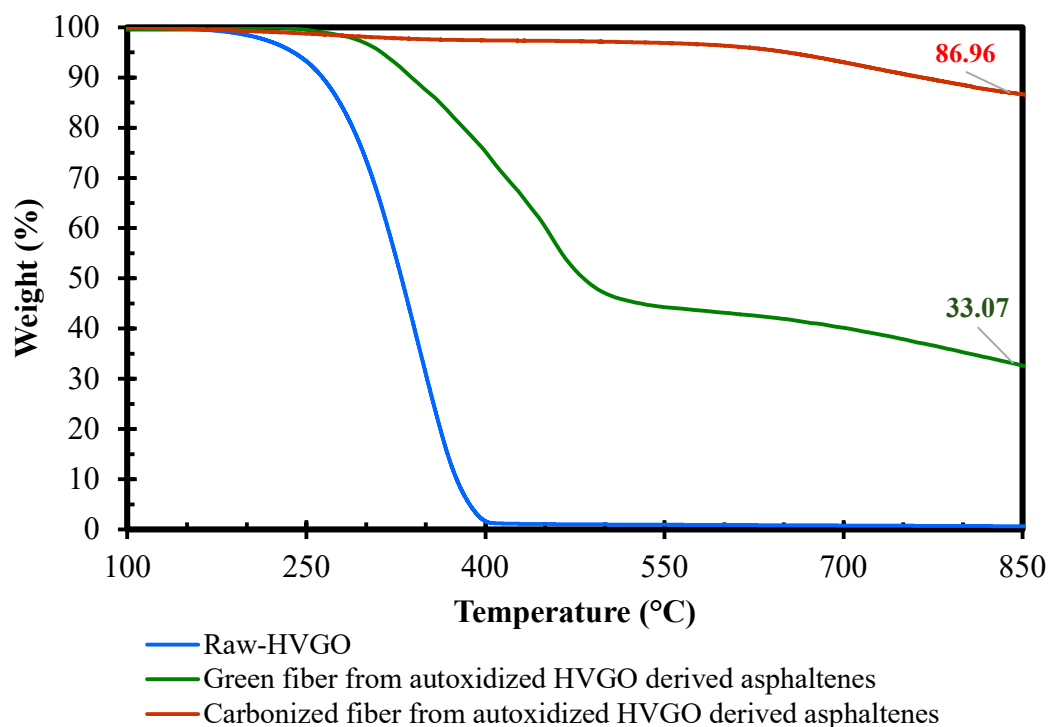


Figure 26. TGA thermograms for Raw-HVGO, green fiber and carbon fiber from autoxidized-HVGO derived asphaltenes.

Thermogram data of carbonized was validated with the literature data, as shown in **Figure 28**, Where it shows a comparison of carbonized fiber from autoxidized HVGO derived asphaltenes and oilsands bitumen derived asphaltenes. Data for the carbonized fiber from oilsands derived asphaltenes was taken from Akash et al.(Akash et al., 2024) From the Figure, it is clear that both values perfectly overlap.

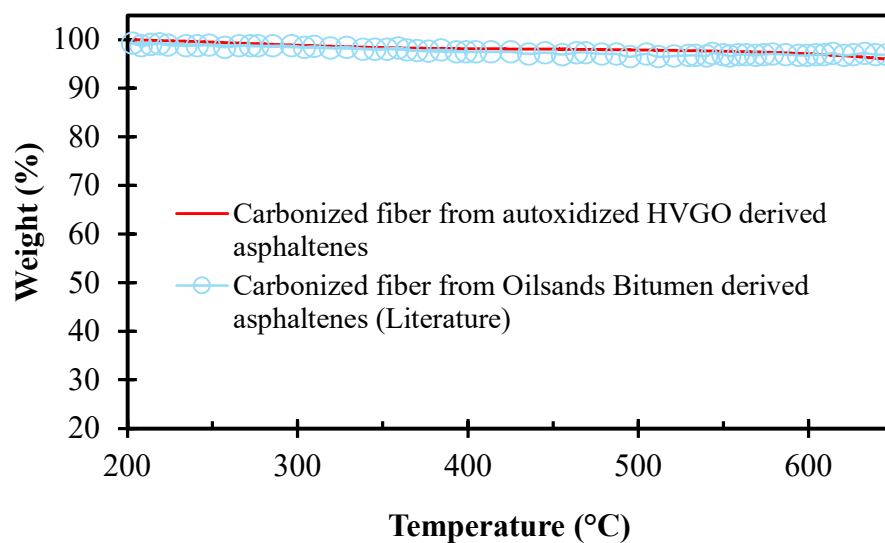


Figure 27 . Comparison of carbon fiber from our study with the available literature data. (Akash et al., 2024).

Overall, while the asphaltene extracted from oxidized HVGO with tetralin shows good potential as a carbon fiber precursor, there are areas for improvement, particularly in achieving higher thermal stability and smaller carbon fiber diameters. Further process refinement could enhance its suitability for high-performance carbon fiber applications and would be a potential scope of future research.

CHAPTER 5

RESULTS AND DISCUSSION: CARBON FIBER FROM VACUUM RESIDUE (VR)

This chapter summarizes the methods used to convert Vacuum Residuum (VR) into carbon fiber precursors. Asphaltenes were synthesized by controlling oxygen levels under varying conditions of temperature, reaction time, and tetralin concentration. The resulting samples were analyzed for key properties, including softening point and thermal stability, to evaluate their suitability for carbon fiber production. The results highlight how optimized methods can transform low-value heavy petroleum fractions like VR into high-quality carbon fiber precursors, making them suitable for industrial applications.

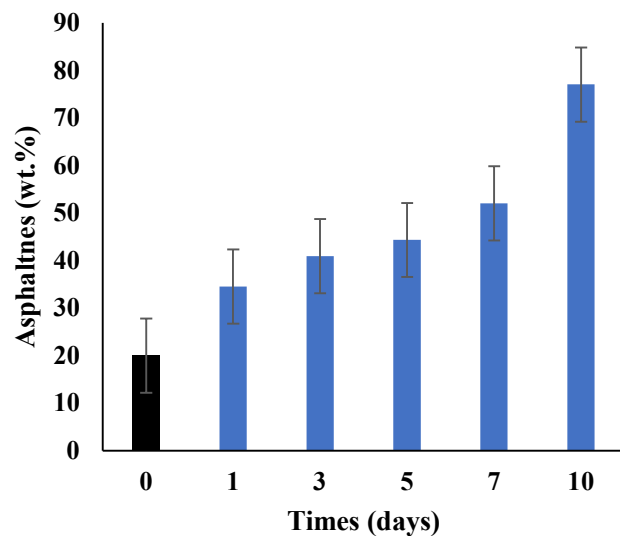
5.1 Change in Asphaltenes Content

Asphaltenes, complex, carbon-rich molecules found in crude oil and bitumen, known for a distinct solubility class. These substances are known for their inability to dissolve in light alkanes like n-heptane, while remaining soluble in aromatic solvents such as toluene. Their high molecular weight and polyaromatic structure make them a valuable source of carbon, particularly suited to the production of carbon fibers. In this section, how temperature, the concentration of naphthenic aromatic hydrocarbons (specifically Tetralin), and reaction time affect the asphaltenes content during the autoxidation of Vacuum Residue (VR) being explored. The data presented in **Table 12** and **Figures 30 and 32** provide key insights into how these factors influence asphaltenes formation.

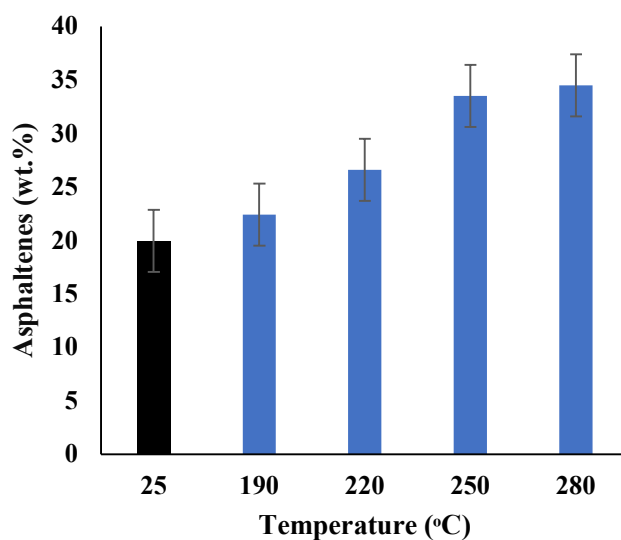
Table 12. A summary of the change in asphaltenes content, viscosity, and softening point during VR autoxidation in the presence of tetralin at different operating conditions.

Experiment ID	Tetralin concentration (% wt.)	Time (days)	Temperature (°C)	Asphaltenes content (wt. %)	Softening point (°C)
A	0	1	190	22.4	-
B	0	1	220	26.6	-
C	0	1	250	33.5	-
D	0	1	280	34.5	-
E	0	3	280	40.9	84.6
F	0	5	280	44.3	-
G	0	7	280	52	112
H	0	10	280	77	191
I	2	1	190	23.1	-
G	4	1	190	30.5	-
K	6	1	190	26.8	-
L	8	1	190	25.2	-
M	4	3	190	43.2	102
N	4	5	190	54.3	126
O	4	7	190	66.9	146
P	4	10	190	73.2	169

The Temperature Effect: In this section, the effect of temperature and reaction time on asphaltenes content during the autoxidation of Vacuum Residue (VR) were examined, as illustrated in **Figure 30 (a)** for temperature at fixed time (1 day) and Figure 29 (b) for time at a constant reaction temperature of 280°C. Both temperature and time significantly influenced asphaltenes production.



[a]



[b]

Figure 28. [a]: Change in asphaltenes content with temperature after one day of autoxidation and [b]: Change in asphaltenes content with time at 280°C.

In **Figure 30 (a)**, the impact of temperature is shown over a constant reaction time of one day. Starting from an initial asphaltene content of 19.97 wt. % in the raw VR, the concentration increased steadily with rising temperature, reaching 26.6 wt. % at 220°C and

peaking at 34.5 wt. % at 280°C. This trend indicates that higher temperatures enhance autoxidation, leading to a greater accumulation of asphaltenes within the VR over a one-day period.

Figure 30 (b) illustrates the effect of reaction time on asphaltenes content at a constant temperature of 280°C. Beginning with 19.97 wt. % in raw VR, the asphaltenes content rose significantly over time, reaching 40.9 wt. % after 3 days and ultimately achieving a maximum of 77 wt. % after 10 days. This time-dependent increase suggests that prolonged exposure to oxidation conditions at high temperature encourages further asphaltenes formation, demonstrating the benefit of extended reaction times for maximizing asphaltenes yield.

Overall, these results demonstrate that both higher temperatures and longer reaction times contribute to increased asphaltenes content during the autoxidation of VR.

Autoxidation is a controlled chemical process where hydrocarbons react with molecular oxygen at relatively low temperatures. Unlike combustion, autoxidation occurs under conditions that allow for a slower, controlled oxidation process, preventing the rapid, exothermic reactions characteristic of burning. The reaction network of aliphatic hydrocarbon autoxidation, shown in **Figure 31**, outlines key stages in this oxidation process. The process begins as aliphatic hydrocarbons react with oxygen to form reactive hydrocarbon free radicals. These free radicals, in turn, proceed along two potential pathways: in oxygen-limited conditions, they can combine with other hydrocarbons to create addition products (Step II), or, if excess oxygen is present (Step III), they react further to form hydroperoxides. Hydroperoxides are inherently unstable and can break

down into alcohols (Step IV) or undergo further oxidation, yielding carbonyl compounds like aldehydes and ketones (Step V). Alcohols produced in this manner can also oxidize further, leading to carboxylic acids.

The formation rate of free radicals is directly influenced by temperature, with higher temperatures accelerating radical formation. At elevated temperatures, the increased concentration of free radicals enhances their likelihood of reacting with one another, forming longer and heavier hydrocarbon products. This process can initiate a chain reaction, where newly formed heavier hydrocarbons themselves become sources of free radicals and continue to produce even larger molecules. Heavier hydrocarbons require more energy to form free radicals compared to lighter ones, yet higher temperatures facilitate this process even for the bulkier molecules, eventually producing compounds categorized as asphaltenes.

Moreover, at a given temperature, allowing the reaction more time increases free radical production, amplifying the likelihood of heavier molecular formations. Extended reaction time at these elevated temperatures thus facilitates further asphaltenes production, as more free radicals accumulate and undergo addition reactions.

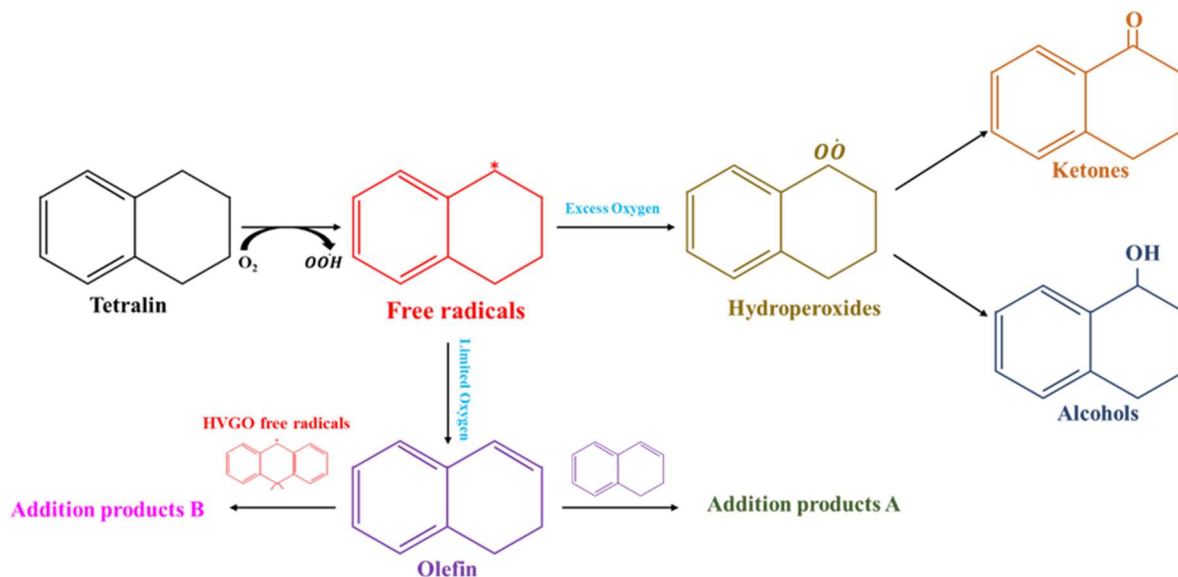
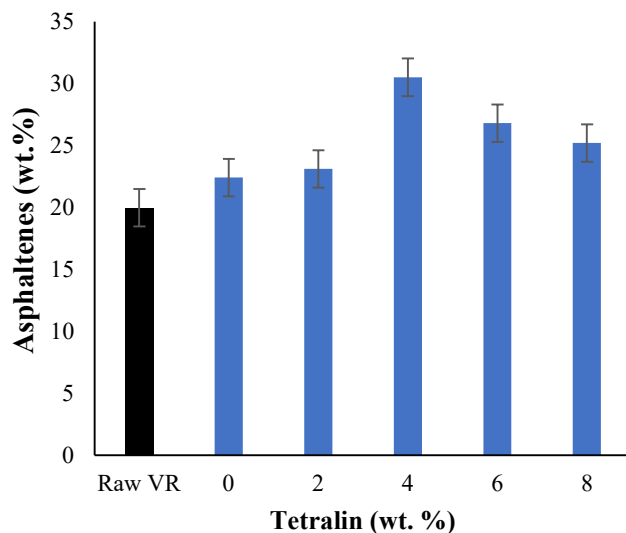


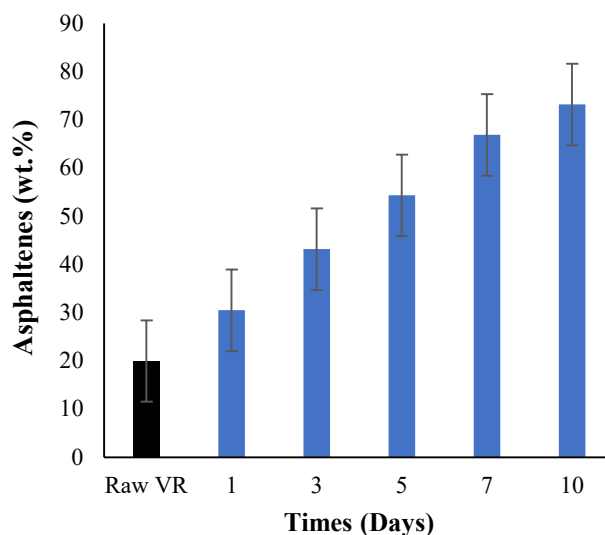
Figure 29. A typical autoxidation reaction of hydrocarbons (Tetralin) pathways

In summary, autoxidation allows hydrocarbons to react with oxygen in a controlled, gradual manner, distinct from combustion. Through free radical formation, hydrocarbons undergo various oxidation steps, leading to heavier compounds like asphaltenes, especially at higher temperatures. Both elevated temperatures and longer reaction times increase free radical formation, enhancing asphaltenes production.

Effect of The Naphthenic Aromatic Hydrocarbons: In this section, the impact of the variation in tetralin concentrations on asphaltenes content during the autoxidation reaction at a temperature of 190°C with a reaction time of one day was explored, as illustrated in **Figure 32 (a)**. Additionally, the effect of reaction time was investigated at a fixed tetralin concentration (4%) and the same temperature of 190°C, providing insights into the time-dependent behavior of asphaltenes formation under these specific conditions, as illustrated in **Figure 32 (b)**.



[a]



[b]

Figure 30. [a]: Change in asphaltenes due to tetralin concentration at 190°C and 1 day and [b]: change of asphaltenes due to time at 190°C and 4 % tetralin.

In **Figure 32 (a)**, the effect of varying tetralin concentrations on asphaltenes content is shown after a reaction time of one day. Without any tetralin addition (0 wt%), the asphaltenes content increased slightly. As the concentration of tetralin rose to 2 wt%, there was a further modest increase. However, at 4 wt% tetralin, the asphaltenes content reached its peak at 30.5 wt%, suggesting an optimal concentration for asphaltenes formation under these conditions. Beyond this point, higher tetralin concentrations led to a decrease in asphaltenes content, dropping to 26.8 wt% at 6 wt% and 25.2 wt% at 8 wt%.

Figure 32 (b) depicts the effect of reaction time on asphaltenes content at a fixed tetralin concentration of 4 wt% and a constant temperature of 190°C. After one day, asphaltene content rose to 30.5 wt% and continued to increase with extended reaction time, reaching 43.2 wt% after 3 days and 54.3 wt% after 5 days. This upward trend persisted, with asphaltenes levels climbing to 66.9 wt% after 7 days and reaching a maximum of 73.2 wt%

after 10 days. The steady rise in asphaltenes content with time suggests that prolonged oxidation encourages additional asphaltenes formation, likely due to continuous free radical reactions.

The concept of adding tetralin during the autoxidation reaction is based on the understanding that naphthenic aromatic hydrocarbons, which are components of heavy oils, have the capacity to react and form heavier addition products during the autoxidation reaction. The reactivity of these hydrocarbons, including tetralin, is influenced by factors such as temperature, reaction time, and oxygen availability during the reaction. As shown in **Figure 31**, the oxidation behavior of tetralin is highly dependent on oxygen levels. In high-oxygen environments, tetralin tends to oxidize into products like alcohols and ketones. However, under conditions with limited oxygen, tetralin primarily forms addition products, a process being confirmed in a previous study where increased viscosity and density were observed as a result of these additions.

5.2 Extent of Heavy Products Formation

The formation of heavy products during VR autoxidation is crucial for evaluating its potential as a high-carbon feedstock, like for carbon fibers. Thermogravimetric analysis (TGA) and softening points were used to assess this. TGA (**as in Figure 31**) reveals thermal stability and weight loss patterns, while softening points (**Tables 6 and 12**) indicate the transition to a pliable state. Together, these metrics highlight how conditions like temperature, reaction time, and tetralin concentration influence the formation and stability of heavy molecular structures in VR.

Figure 31 presents the TGA curves for raw VR, oxidized VR samples under different conditions, and VR-derived asphaltenes, highlighting their thermal stability. Raw VR showed significant weight loss, with only 14% of its original weight remaining at 800°C, indicating its relatively volatile nature. In contrast, the oxidized VR samples retained between 19% and 24% of their weight at 800°C, demonstrating improved thermal stability due to the formation of heavier, more stable compounds. The VR-derived from raw asphaltenes exhibited the highest stability, retaining around 35% of their weight at 800°C. This indicates that asphaltenes are the most thermally robust products, likely due to their complex, high-molecular-weight structure formed during the autoxidation process.

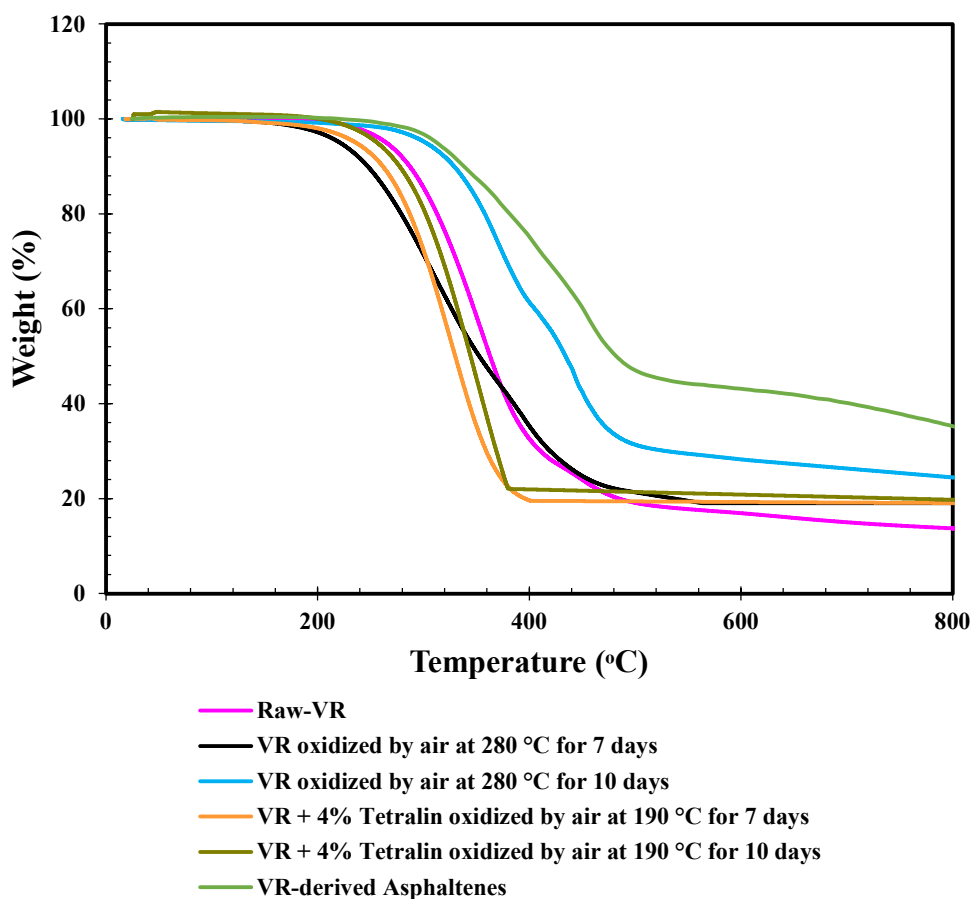


Figure 31. TGA thermograms for raw- and oxidized-VR and it's derived asphaltenes at different operating conditions.

Using the softening point of raw VR at 54°C as a baseline (**Table 6**), the data in **Table 12** show a significant increase in softening points for oxidized VR samples, highlighting the development of more rigid, complex structures through autoxidation. As oxidation progresses, either through increased temperature or extended reaction time, the softening point consistently rises, indicating enhanced structural rigidity. For example, VR samples oxidized at 280°C reached a softening point of 84.6°C after 3 days, further increasing to 191°C after 10 days. Similarly, VR samples oxidized with 4% tetralin at 190°C exhibited a rise in softening point from 102°C after 3 days to 169°C after 10 days, indicating that

both tetralin concentration and oxidation duration play key roles in reinforcing the material structure. The VR-derived asphaltenes, with a softening point of 195°C, stand out as the most rigid and thermally stable, confirming the formation of highly complex, high-molecular-weight compounds.

The previously discussed reasons for increased thermal stability and softening points are prolonged oxidation time and elevated temperature which hold true here. However, an intriguing observation is that the VR samples with 4% tetralin at 190°C reached softening point and stability values similar to those of VR samples oxidized at 280°C without tetralin. This effect can be attributed to the reactive nature of naphthenic aromatic hydrocarbons, which are known to be particularly susceptible to autoxidation reactions under moderate conditions.

Adding tetralin to VR effectively raises the concentration of these reactive components within the mixture, thereby enhancing the reactivity of VR toward oxidation and facilitating the formation of heavier products. Our previous research demonstrated that tetralin can form addition products even at a lower temperature of 130°C, with product formation directly proportional to reaction time. In the present experiments, oxidation at an even higher temperature of 190°C, with extended durations up to 10 days, providing ideal conditions for significant structural transformation is conducted

In contrast, pure VR has an H/C ratio of 1.36, indicating a relatively high proportion of lighter fractions and a lower content of naphthenic aromatics (1.5 mean higher concentration of naphthenic aromatic hydrocarbons), which are less reactive under similar conditions. This reduced reactivity makes pure VR less prone to forming heavy products

compared to VR samples with added tetralin. Therefore, the VR samples with 4% tetralin at 190°C could achieve stability and softening characteristics comparable to those of VR oxidized at 280°C without tetralin. This finding highlights the role of naphthenic aromatics like tetralin in accelerating the autoxidation process and enhancing the formation of high-molecular-weight, thermally stable products even at relatively lower temperatures.

5.3 Elemental and Structural Analysis of VR and Oxidized VR

The elemental composition and FTIR spectroscopy results collectively highlight the chemical and structural changes in VR and its oxidized derivatives under various treatment conditions. **Table 13** demonstrates that oxidation increases oxygen content and reduces the H/C ratio, reflecting enhanced aromaticity and diminished aliphatic content. Prolonged oxidation at higher temperatures (e.g., 280°C for 10 days, Sample H) results in the most significant aromatization, as indicated by the lowest H/C ratio (1.28). This can be attributed to extensive dehydrogenation and oxygen incorporation into the VR structure during oxidation, leading to the formation of stable aromatic compounds. The asphaltenes extracted from VR exhibit the highest carbon content (84%) and the lowest H/C ratio (1.0), reflecting their highly condensed aromatic structure. These asphaltenes likely represent the most thermally and chemically stable fraction of the VR, having undergone significant condensation and dehydrogenation during extraction and oxidation. Their presence highlights the endpoint of the oxidative transformation process, further underscoring the progressive shift toward aromaticity in VR under these conditions.

Table 13. Elemental composition (wt.%) VR and oxidized VR.

Samples	ID	C	H	S	N	O	H/C
VR	-	81.9	9.3	6.8	1.5	0.4	1.4
VR_ 280°C, 7 Days	G	81.8	9.4	6.7	0.7	2.6	1.4
VR + 4 % Tetralin_ 190°C, 7 Days	O	81.6	9.2	4.2	1.1	3.8	1.3
VR_ 280°C, 10 Days	H	82.8	9.2	5.5	0.1	2.4	1.3
VR + 4 % Tetralin_ 190°C, 10 Days	P	82.2	9.2	4.4	0.9	3.2	1.3
Asphaltenes extracted from VR	-	84	7	6.7	1.1	0.9	1

FTIR spectra (**Figure 32**) further support these findings, showing a gradual disappearance of aliphatic C-H peaks and the emergence of strong aromatic C=C stretching vibrations as oxidation progresses. Samples treated with tetralin exhibit reduced sulfur content and slightly moderated aromatic condensation, as observed in the spectra for 190°C oxidation. The presence of tetralin likely acts as a hydrogen donor, stabilizing reactive species and preventing excessive cross-linking, which explains the lower intensity of aromatic peaks compared to untreated oxidized samples. Asphaltenes, extracted from VR, show the highest carbon content and dominant aromaticity, representing the end stage of oxidation with extensive condensation and dehydrogenation.

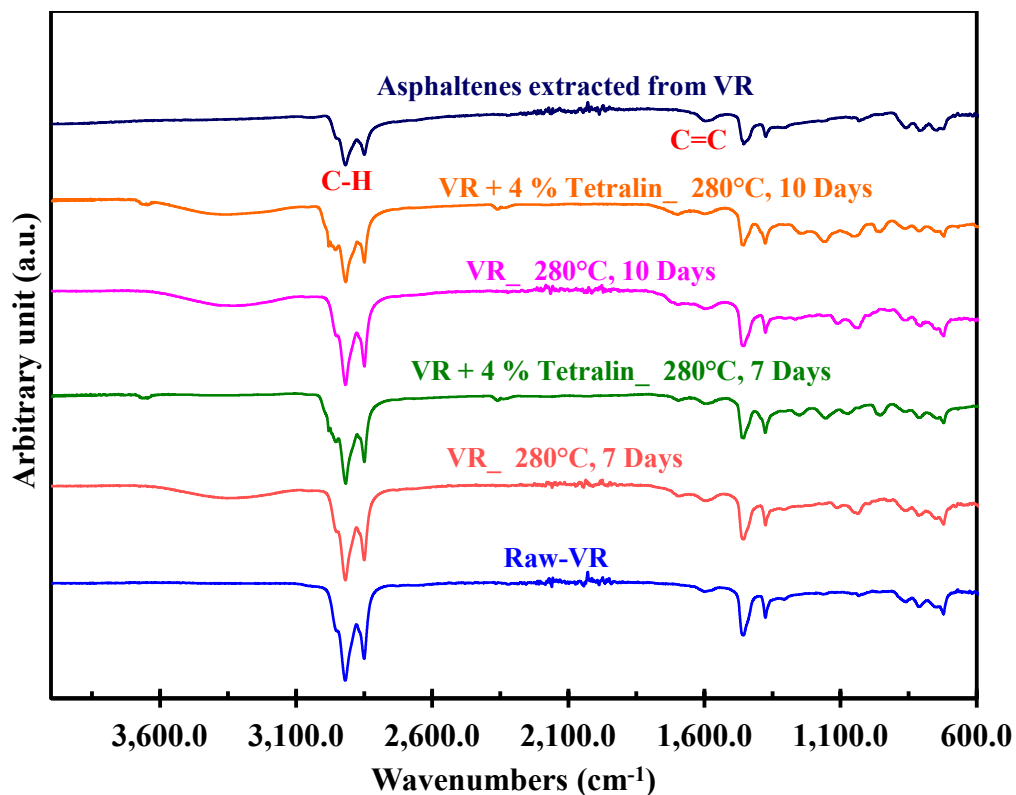


Figure 32. FTIR spectrum of oxidized VR and VR-derived asphaltenes

5.4 The suitability of Oxidized VR as Carbon Fiber Precursors

The objective of this section to evaluate the produced samples as viable carbon fiber precursors, by assessing their spinnability using a melt spinning machine and conducted subsequent processing steps, including acid treatment, oxidative stabilization, and high-temperature carbonization. These steps are essential to convert the precursors into carbon fiber. The final carbonized products were then characterized for thermal stability and carbon content, two critical indicators of fiber quality and suitability for high-performance applications.

Table 14 provides a comparative analysis of green fibers produced from various vacuum residue (VR) sources under different oxidation and melt spinning conditions. Key metrics

include fiber diameter, carbon content, and surface characteristics, shedding light on how oxidation duration, temperature, and the addition of tetralin impact the physical and chemical properties of the resulting fibers.

Table 14. Properties of green fiber and melt spinning conditions.

Source of green fiber	melt spinning conditions (°C)	Green fiber diameter (μm)	Carbon (C) content (wt %)	Observation
VR-derived asphaltenes	230 °C, 200 kPa & 500 rpm	50-70	84	-some voids -smooth surface
VR oxidized by air at 280 °C for 7 days	150 °C, 250 kPa & 400 rpm	60-80	81.8	-no void in fibers -smooth surface
VR oxidized by air at 280 °C for 10 days	- ^a	- ^a	82.8	- ^a
VR + 4% Tetralin oxidized by air at 280 °C for 7 days	- ^b	- ^b	82.6	- ^b
VR+ 4% Tetralin oxidized by air at 280 °C for 10 days	180 °C, 300 kPa & 400 rpm	66-85	82.2	-no void in fibers -smooth surface
^a not spinnable material (no filament observed at the above melt spinning condition).				
^b not spinnable material (form liquid droplet at the above melt spinning condition)				

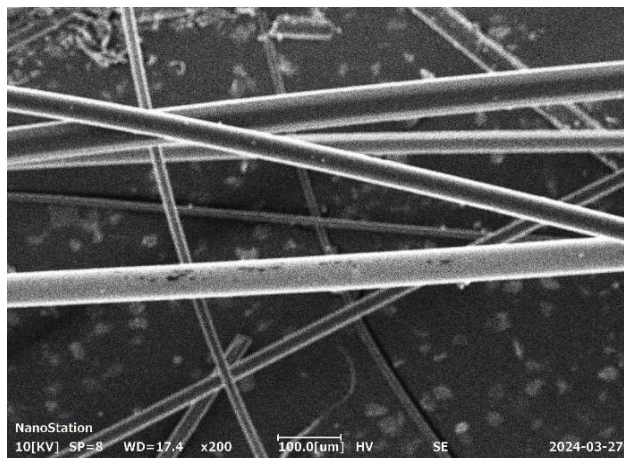
As in **Table 12**, green fibers from VR-derived asphaltenes, spun at 230°C, had diameters of 50-70 μm with a carbon content of 84 wt%, though some bubbles were present as illustrated in **Figure 33**.



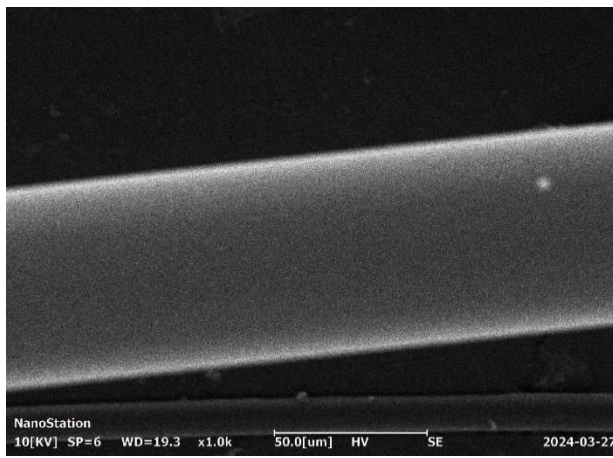
(a)



(b)



(c)



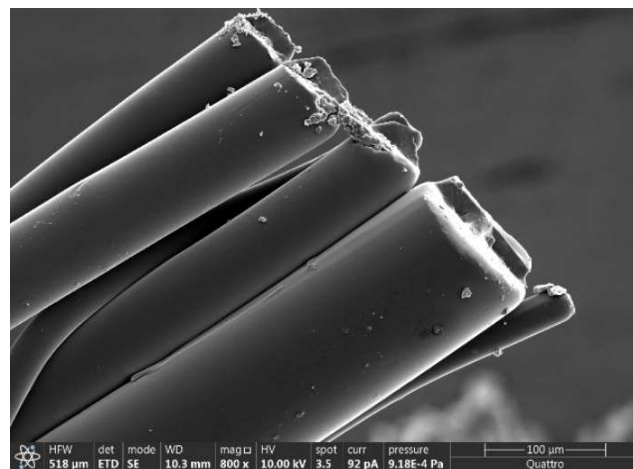
(d)

Figure 33. SEM images of green fiber from VR derived asphaltenes.

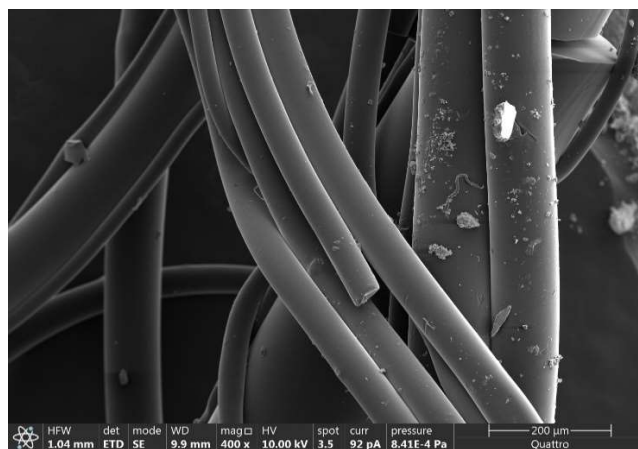
VR oxidized at 280°C for 7 days, spun at a lower temperature (150°C), produced slightly larger, smooth-surfaced fibers (60-80 μm) with 81.8 wt% carbon content, indicating improved integrity (**Figure 34**).



(a)



(b)



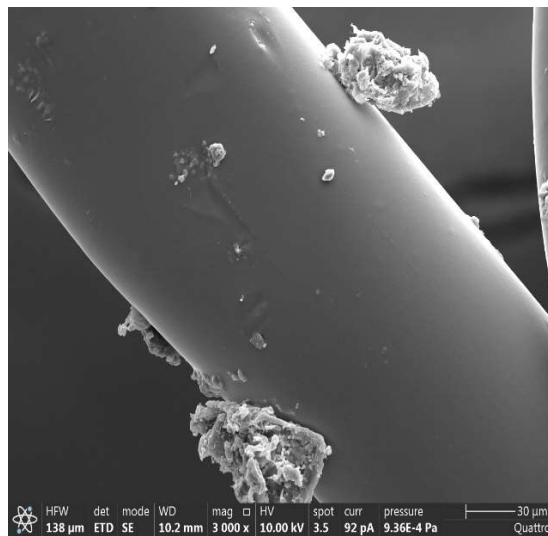
(c)

Figure 34. SEM images of green fiber of oxidized VR (7-days).

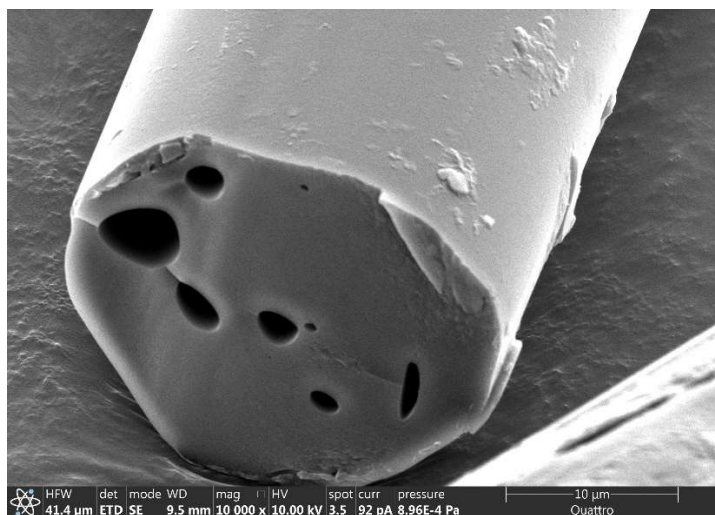
However, samples oxidized at 280°C for 10 days or with 4% tetralin for 7 days were unspinnable, suggesting that these conditions altered material properties, making them unsuitable for fiber formation. The sample with 4% tetralin oxidized at 280°C for 10 days, spun at 230°C, yielded the largest fibers (66-85 μm) and a smooth, void-free surface with 82.2 wt% carbon, showing that tetralin and longer oxidation enhanced fiber quality as in **Figure 34**.



(a)



(b)



(c)

Figure 35. SEM images of green fiber of VR+ 4% Tetralin oxidized by air at 280 °C for 10 days.

The spinnability of the samples is a crucial criterion for determining their suitability as carbon fiber precursors. Among the various materials tested, asphaltene, regardless of their source, are widely recognized in the literature as a primary choice for carbon fiber production. This preference is due to several inherent properties of asphaltene that make them ideal for this purpose.

Asphaltenes exhibit enhanced thermal stability, as demonstrated in Figure 6, allowing them to withstand the high temperatures required during carbon fiber processing. This stability is largely attributed to their rich aromatic content, as shown in the FTIR spectrum (**Figure 32**), where asphaltenes display a broad peak in the aromatic C=C stretch region (1500–1600 cm^{-1}) and only small peaks in the aliphatic C–H stretch region (2800–3000 cm^{-1}), indicating a predominantly aromatic structure with minimal aliphatic content. Additionally, asphaltenes have a relatively high carbon content, as indicated in **Table 14**, which suggests a high molecular weight and improved homogeneity which are both desirable properties for carbon fiber precursors.

However, a notable issue observed in the asphaltenes-derived green fibers was the presence of bubbles within the fiber structure, as shown in **Figure 33 (b)**. These bubbles likely result from gases, such as carbon dioxide, hydrogen sulfide, and oxygen, that attempt to escape during the melt-spinning process, which is conducted under high temperature and pressure in a nitrogen environment. Despite this minor drawback, the inherent properties of asphaltenes including thermal stability, high aromatic content, and carbon-rich composition, make them highly suitable as carbon fiber precursors.

For the other samples that demonstrated spinnability, specifically, VR oxidized by air at 280°C for 7 days and VR with 4% Tetralin oxidized by air at 280°C for 10 days, which they exhibited thermal stability and carbon content comparable to asphaltenes, with a carbon content around 82%, indirectly suggesting a high molecular weight. These attributes collectively contribute to the suitability of these samples as carbon fiber precursors, as they offer a stable base for fiber formation.

The sample of VR with 4% Tetralin oxidized by air at 190°C for 7 days showed only droplet formation during the melt-spinning process, indicating it was unsuitable for green fiber production. This lack of spinnability is likely due to its low softening point, which reflects low viscosity and molecular weight which are characteristics that prevent the material from forming continuous fibers.

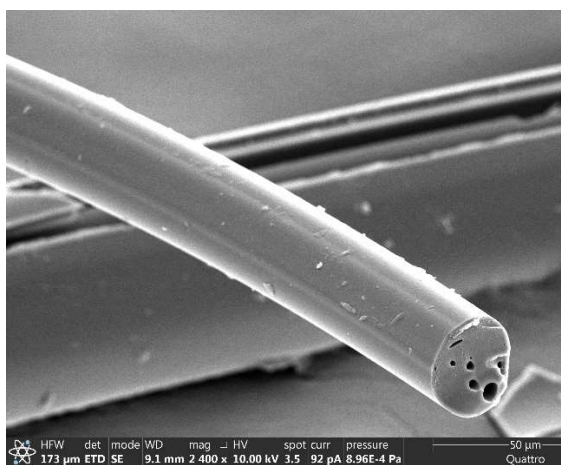
In contrast, VR oxidized by air at 280°C for 10 days exhibited improved thermal stability and other desirable properties compared to the same sample oxidized for 7 days. However, it was still unspinnable, likely due to the increased mesophase concentration resulting from the extended oxidation time. This higher mesophase content can make the material more rigid and inhibit its flow, thus hindering the sample's spinnability. These observations highlight that, while prolonged oxidation can enhance certain properties, an optimal balance is necessary to maintain spinnability for green fiber production.

Table 15. Carbon fiber production conditions and characteristic of carbon fiber from VR.

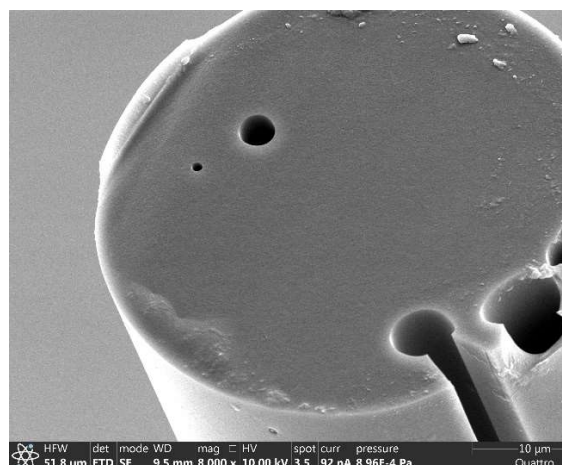
Sample	Acid treatment	Oxidative stabilization	Carbonization	Features
VR-derived asphaltenes	40 wt. % Nitric Acid 20 min residence time	Temperature : 320°C. Air flow rate: 300 ml/min. Time: 27 hours	Temperature : 1000°C. Nitrogen flow rate: 300 ml/min. Time: 0.5 hours	-diameter: 40µm -some voids -92.6 % Carbon
VR oxidized by air at 280 °C for 7 days	40 wt. % Nitric Acid 20 min residence time	Temperature : 200°C. Air flow rate: 300 ml/min. Time: 24 hours	Temperature : 900°C. Nitrogen flow rate: 300 ml/min. Time: 0.5 hours	-no continuous fiber produced -87 % Carbon
VR+ 4% Tetralin oxidized by air at	40 wt. % Nitric Acid	Temperature : 200°C.	Temperature : 900°C.	- no continuous fiber produced

280 °C for 10 days	20 min residence time	Air flow rate: 300 ml/min. Time: 24 hours	Nitrogen flow rate: 300 ml/min. Time: 0.5 hours	-89 % Carbon
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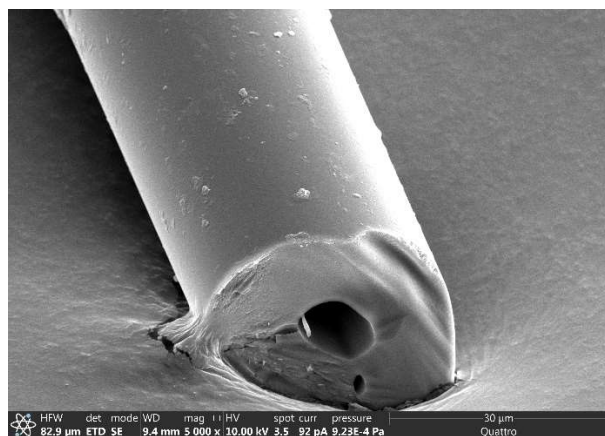
Table 14. outlines the final processing steps for carbon fiber precursors derived from VR samples, focusing on acid treatment, oxidative stabilization, and carbonization conditions. VR-derived asphaltenes, treated at higher stabilization (320°C) and carbonization (1000°C) temperatures, successfully produced carbon fibers with a 40 µm diameter and 92.6% carbon content, though with some voids (**Figure 36**). In contrast, VR oxidized at 280°C for 7 days and VR with 4% tetralin oxidized for 10 days, both stabilized and carbonized at lower temperatures (200°C and 900°C, respectively) as illustrated in **Figure 37 and 38 respectively**, failed to produce carbon fibers despite high carbon content (87–89%). This suggests that high stabilization and carbonization temperatures are essential for achieving the structural integrity required for carbon fiber formation in VR-based materials.



[a]



[b]



[c]

Figure 36. SEM images of Carbon fiber from raw VR derived asphaltenes.

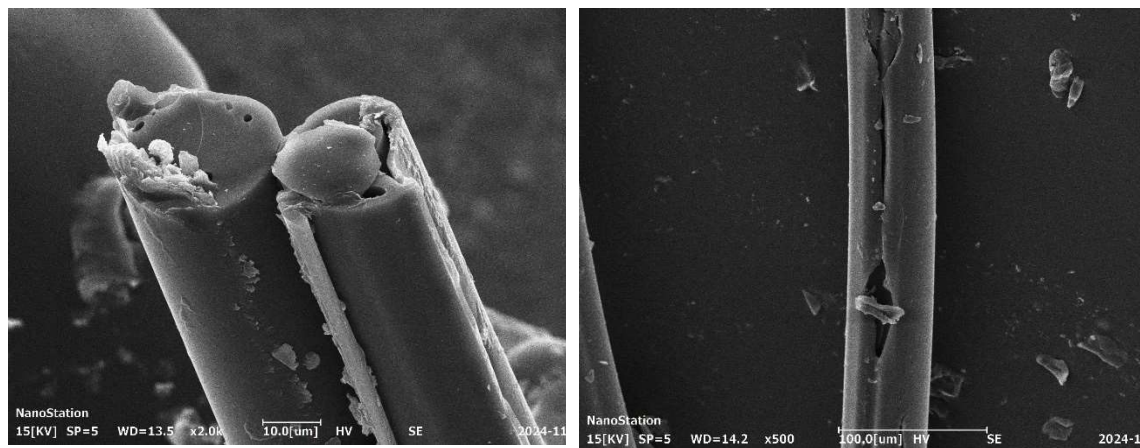


Figure 37. SEM of carbonized VR Oxidized for 7 days at 280°C

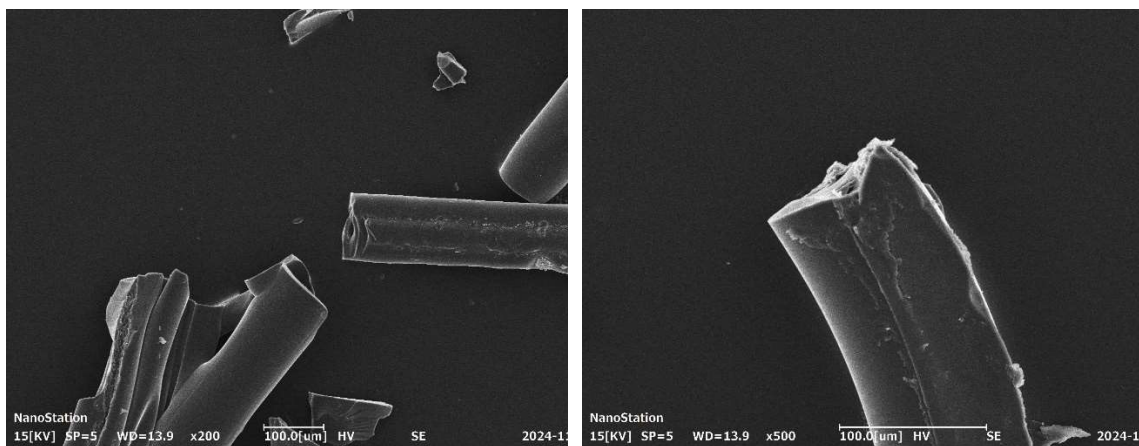


Figure 38. SEM of carbonized VR+ 4 % Tetralin oxidized for 10 days at 190°C.

The primary reason that fibers directly spun from oxidized vacuum residue (VR) do not form continuous structures is due to the presence of other components mixed with asphaltenes, such as saturates, aromatics, and resins. During the high-temperature carbonization process (around 900°C), these lighter components tend to evaporate, leaving behind an incomplete structure that lacks the integrity of a continuous fiber. Despite this limitation, the samples still exhibit relatively high carbon content and thermal stability, as demonstrated in **Figure 39**, highlighting their potential suitability as carbon-rich materials for applications where continuous fiber formation is not critical.

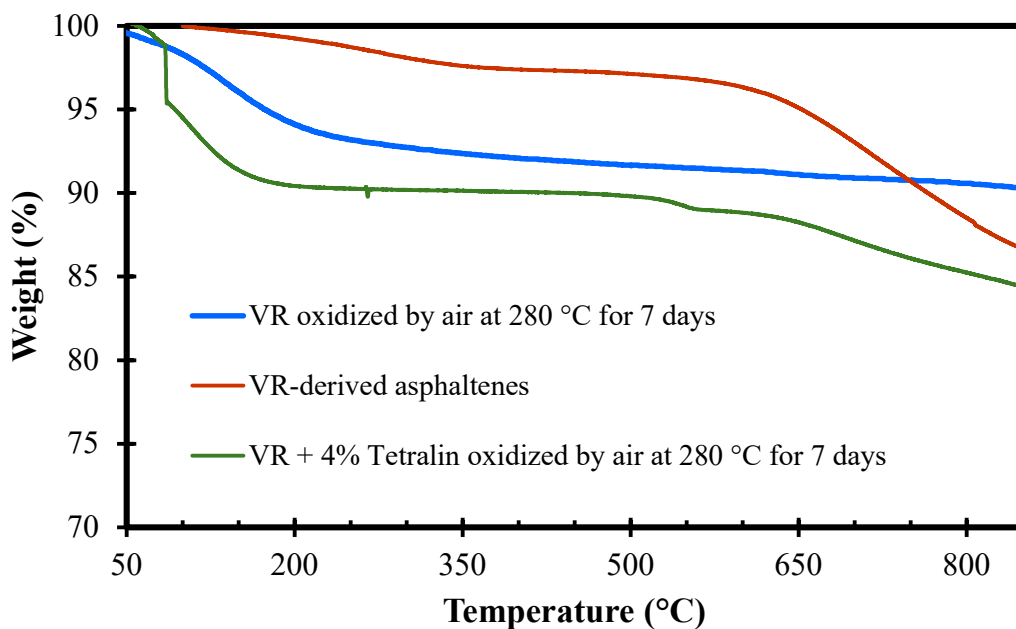


Figure 39. TGA thermograms for carbonized samples.

Overall, this study highlights the process of converting vacuum residue (VR) into carbon fiber precursors through carefully controlled oxidation, followed by melt-spinning and high-temperature treatments. Key findings indicate that high stabilization and carbonization temperatures are essential for forming continuous, structurally sound carbon fibers. Oxidized VR, especially with added tetralin, produced green fibers with improved carbon content and thermal stability. However, lower processing temperatures or extended oxidation time resulted in non-continuous fibers due to the evaporation of lighter components, underscoring the importance of precise temperature and component control to achieve continuous, high-quality carbon fibers.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

Heavy vacuum gas oil (HVGO) and vacuum residue (VR), as low-value by-products of the petroleum refining process, hold untapped potential as carbon fiber precursors. This study aimed to transform these heavy petroleum fractions into valuable materials through a controlled autoxidation process, evaluating how factors like oxygen addition methods, temperature, oxidation time, and the presence of naphthenic-aromatic hydrocarbons (specifically tetralin) impact key properties required for carbon fiber production. The research highlights the conditions under which HVGO and VR can achieve enhanced asphaltene content, increased viscosity, softening points, and thermal stability, thereby demonstrating their viability as carbon-rich precursors for carbon fiber applications.

6.1 Conclusions

- **Effectiveness of Autoxidation:** Autoxidation proved highly effective in increasing asphaltene content in both HVGO and VR, both of which initially contained minimal asphaltenes. The method of oxygen addition significantly influenced the results. In HVGO, air blowing without mixing at higher temperatures (190°C) and extended oxidation times produced the maximum asphaltene content, reaching 47.2 wt.% after 72 hours with the addition of 5% tetralin. Conversely, for more uniform oxidation at lower temperatures, air bubbling with mixing was more effective. For VR, the highest asphaltene yield (77 wt.%) was achieved by oxidizing at 280°C for

10 days, resulting in a high-molecular-weight product with a softening point of 191°C, qualities ideal for carbon fiber production due to the product's enhanced thermal stability.

- **Role of Tetralin Addition:** Tetralin, a naphthenic-aromatic hydrocarbon, further enhanced the effectiveness of autoxidation, especially under controlled conditions. In HVGO, which initially had negligible asphaltenes, adding 5% tetralin under autoxidation conditions at 190°C for 72 hours resulted in maximum asphaltene content (47.2 wt.%), viscosity (117.6 Pa.s), and softening point (210°C), with air blowing being particularly effective. • In VR, the highest asphaltene yield (77 wt.%) was achieved with 10-day oxidation at 280°C, yielding a softening point of 191°C. VR samples with 4% tetralin, oxidized at a milder 190°C for 10 days, also exhibited significant stability (73.2 wt.% asphaltenes and a softening point of 169°C), demonstrating tetralin's effectiveness in milder conditions.
- **Fiber Quality and Spinnability in HVGO- and VR-Derived Precursors:** The optimized conditions for autoxidation and tetralin addition in both HVGO and VR enhanced the spinnability of the asphaltenes-rich products. HVGO-derived asphaltenes, oxidized with tetralin, produced green fibers with a diameter around 70 µm. VR-derived asphaltenes, spun at 230°C, resulted in green fibers with diameters of 50–70 µm and a carbon content of 84 wt%. VR samples oxidized at 280°C for 7 days formed smooth green fibers (60–80 µm) when spun at 150°C, while VR oxidized with 4% tetralin at 280°C for 10 days yielded larger fibers (66–85 µm) when spun at 180°C.

- **Fiber Quality and Carbonization:** After carbonization, HVGO-derived fibers reduced to diameters of 40–50 μm , achieving 92.6 wt % carbon content. VR-derived fibers, spun at 230°C and carbonized at 1000°C, retained similar diameters and carbon content, while VR samples oxidized at 280°C for 7 days or with 4% tetralin for 10 days did not form continuous fibers after carbonization at 900°C due to evaporative losses from lighter components.

6.2 Recommendations

- **Investigation of the role of additional naphthenic-aromatic hydrocarbons, including indene and indan, during pretreatment:** Explore other compounds to potentially enhance asphaltene formation and thermal stability, further improving spinnability and fiber formation.
- **Utilization of purified asphaltenes for fiber production:** Enhance the quality of carbon fibers by purifying VR- and HVGO-derived asphaltenes with toluene to remove unwanted components, which could lead to better spinnability and fiber quality.
- **Investigation of chemical modifications occurring throughout the pretreatment procedure:** Use Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) coupled with positive APPI (atmospheric pressure photoionization) and positive ESI (electrospray ionization) ionizers to differentiate the nonpolar and polar parts of asphaltenes. This analysis will offer insights into asphaltenes behavior during carbon fiber processing.

- **Utilization of various spinneret sizes to produce carbon fibers of differing diameters:** Test additional spinneret sizes (30, 60, and 90 micrometers) on the melt-spinning machine to assess their effect on fiber quality, as only a 150-micrometer spinneret was used in this study.
- **Characterization of carbon fibers through supplementary techniques to assess carbon fiber quality:** Perform tensile strength and modulus testing, along with electrical characterization of the fibers, to provide a more comprehensive assessment of their properties and potential applications.
- **Assessment of composite production to address challenges associated with carbon fiber manufacturing and enhance their properties:** In future research phases, explore the development of carbon fiber composite materials, which could leverage the unique properties of carbon fibers for enhanced structural and functional applications.
- **Assessment of the utilization of produced precursors for the generation of additional value-added products, including graphene and carbon nanotubes:** Consider further applications of asphaltenes derived from VR, oxidized VR, and Oxidized HVGO, such as the production of graphene and carbon nanotubes, to fully capitalize on their carbon-rich nature and structural potential for advanced materials.

These conclusions and recommendations provide a foundation for advancing the use of heavy petroleum fractions in producing high-performance carbon fibers and other carbon-based materials, thus promoting sustainable, cost-effective solutions in materials science.

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Vitae

Name :Mustafa Mohammed Ali Amin |

Nationality :Sudanese |

Date of Birth :7/25/1997|

Email :aminmustafa289@gmail.com|

Address :11111, Khartoum Bahri, Khartoum, Sudan|

Academic Background :Bachelor degree in Chemical Engineering, University of
Khartoum, Sudan 2020|

Publications

Peer Review Manuscripts:

- **Amin, M. M.**; Mohamed, L. S.; Hossain, M. M.; Razzak, S. A.; Siddiquee, M. N. Prospects and Challenges of Carbon Fiber Production from Heavy Petroleum Fractions. *Ind. Eng. Chem Res.* 2024, 63, 36, 15613–15636. <https://doi.org/10.1021/ACS.IECR.4C01136>.
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APPENDIX



Figure 41. Raw HVGO

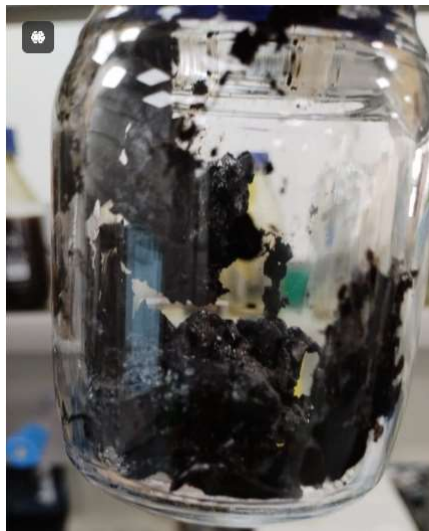


Figure 40. Oxidized HVGO + 5 % tetralin, 190°C.



Figure 42. Raw VR



Figure 43. Asphaltenes from Oxidized HVGO + 5 % tetralin, 190°C.



Figure 44. Setup of the autoxidation experiment.



Figure 45. Melt-spinning Machine.



Figure 46. Oxidative stabilization furnace



Figure 47. Carbonization furnace