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Sustainable biofuel production from oleaginous crops in Kenya

Characterization of local oleaginous feedstocks: Croton megalocarpus and waste cooking oil for biofuels production

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Abstract

Kenya is experiencing a rapid economic growth, with a population growth rate of 2% annually and an urbanization rate increasing by 3.7% per year. This has led to rising energy demand and a significant increase in CO2 emissions. The national energy mix is dominated by biomass (62.5%), petroleum products (18.5%), and renewables (16.9%). Although transport accounts for only 21.7% of final energy consumption, it is responsible for 62% of CO2 emissions and consumes 76% of petroleum products, primarily diesel and gas oil (51%). Kenya's heavy reliance on petroleum imports is striking, domestic oil production is nonexistent, and net imports cover 123.2% of final petroleum consumption. From 2000 to 2021, imports rose by 274%, accounting for 91% of the country's total energy imports. Considering these challenges, the development of alternative fuels is critical to reducing fossil fuel dependence, diversifying the energy mix, improving energy security, and lowering greenhouse gas emissions. In this context, this study aims to characterize two local oleaginous feedstocks, Croton megalocarpus oil and waste cooking oil, to assess their suitability for biodiesel production. While sustainable biofuels are key to the energy transition, it's essential to manage competition with food production and ensure the sustainable use of land and water resources. Among promising solutions, Croton megalocarpus, a native species to sub-Saharan Africa that thrives on marginal land with minimal water, offers significant potential. Similarly, urbanization and population growth are increasing the availability of waste cooking oil. Often discarded as waste, it can be collected and transformed into a valuable resource for biofuel production if an efficient infrastructure is established. To assess the potential of these feedstocks, detailed tests were conducted to characterize their chemical and physical properties using GC-MS (Gas Chromatography-Mass Spectrometry) and FTIR (Fourier Transform Infrared Spectroscopy), measuring parameters such as acidity, density, viscosity, calorific value, moisture content, saponification number, peroxide value, iodine number, and cloud point. These results were compared with those of more established feedstocks like Jatropha and Ricinus, providing insight into the feasibility of using these oils for biofuel production. Following the characterization, lab-scale *experiments were carried out to explore the challenges of converting vegetable oils into biodiesel via transesterification with basic catalysts. Following lab experiments on transesterification for biodiesel production using the same oleaginous feedstock, this study also examines the theoretical requirements for producing a different class of biofuels: Lipid-based Renewable Hydrocarbons such as HVO (Hydrotreated Vegetable Oil) and HEFA (Hydroprocessed Esters and Fatty Acids). These hydrocarbons offer significant advantages over biodiesel due to their non-oxygenated nature, making them fully compatible with existing fuel infrastructure without blending constraints, while still contributing to the transition towards renewable energy sources. Overall, the study demonstrates that the sustainable utilization of local resources, such as Croton and waste cooking oil, presents a viable pathway for Kenya to reduce its energy dependence, foster a sustainable biofuel industry, and promote economic and environmental development without compromising food production or land use.*

Abstract (italian version)

In Kenya, una rapida crescita demografica (+2% annuo) ed un tasso di urbanizzazione in aumento (+3,7% annuo) alimentano una crescente domanda energetica ed un conseguente aumento delle emissioni di CO2. Il mix energetico nazionale (Total Energy Supply, TES) è dominato da biomassa (62,5%), prodotti petroliferi (18,5%) e fonti rinnovabili (16,9%). Sebbene il settore dei trasporti rappresenti solo il 21,7% del consumo energetico finale, è responsabile del 62% delle emissioni di CO2 e utilizza il 76% dei prodotti petroliferi, principalmente sotto forma di gasolio e diesel (51%). La dipendenza del Kenya dalle importazioni di petrolio è considerevole: la produzione interna di petrolio è nulla e le importazioni nette coprono il 123,2% del consumo finale di prodotti petroliferi. Tra il 2000 e il 2021, le importazioni di petrolio sono aumentate del 274%, con il 91% del totale delle importazioni energetiche del paese derivante da prodotti petroliferi. In questo scenario, lo sviluppo di carburanti alternativi è cruciale per ridurre la dipendenza dai combustibili fossili, offrendo un'opportunità per diversificare il mix energetico del Kenya, migliorare la sicurezza energetica e ridurre le emissioni di gas serra. In questo contesto, questo studio ha come obiettivo la caratterizzazione di due materie prime locali, l'olio di Croton megalocarpus e l'olio vegetale usato, al fine di valutarne il potenziale per la produzione di biodiesel e HVO (Hydrotreated Vegetable Oil). Sebbene i biocarburanti sostenibili rappresentino una soluzione indispensabile nella transizione energetica, è necessario che la possibile competizione con la produzione alimentare, l'utilizzo sostenibile del suolo e delle risorse idriche siano adeguatamente gestite. Tra le possibili soluzioni, il Croton megalocarpus, una specie endemica dell'Africa subsahariana che cresce su terreni marginali e richiede quantità minime di acqua, rappresenta una promettente alternativa sostenibile. Per quanto riguarda l'olio vegale usato, la crescita demografica e l'urbanizzazione stanno incrementando la produzione di questa risorsa. Attualmente considerato uno scarto, se raccolto attraverso un'infrastruttura efficiente, può essere trasformato in una risorsa valorizzabile per la produzione di biocarburanti derivanti da feedstocks oleaginosi. Al fine di esplorare le potenzialità di questi feedstocks, sono stati condotti test approfonditi per caratterizzarne la composizione e le proprietà chimico-fisiche, utilizzando strumenti *come GC-MS (Gas Chromatography-Mass Spectrometry) e FTIR (Fourier Transform Infrared Spectroscopy), e misurando parametri chiave quali acidità, densità, viscosità, potere calorifico, contenuto di umidità, numero di saponificazione, valore di perossido, numero di iodio e cloud point. Questi risultati sono stati confrontati con quelli di oli vegetali ottenuto da feedstocks più utilizzati, come Jatropha, Ricinus, e altri, per comprendere il potenziale di questi oli vegetali nella produzione di biocarburanti. Successivamente alla caratterizzazione, sono stati condotti esperimenti su scala di laboratorio per comprendere meglio le criticità della trasformazione degli oli vegetali in biodiesel attraverso il processo di transesterificazione in presenza di catalizzatori basici. Parallelamente, è stato effettuato uno studio teorico sulla di una classe differente di biocarburanti: idrocarburi rinnovabili di origine lipidica, come HVO (Hydrotreated Vegetable Oil) e HEFA (Hydroprocessed Esters and Fatty Acids). Questi idrocarburi offrono vantaggi significativi rispetto al biodiesel, poiché, essendo non ossigenati, sono pienamente compatibili con le infrastrutture esistenti senza necessità di miscelazione. L'analisi condotta dimostra complessivamente come l'uso sostenibile di risorse locali, quali Croton e olio vegetale usato possano fornire una soluzione sostenibile per il Kenya, riducendo la dipendenza energetica e favorendo lo sviluppo di una filiera di biocarburanti che non comprometta la produzione alimentare o l’uso del suolo, ma anzi favorisca lo sviluppo sostenibile.*

Desidero ringraziare il mio relatore, il professor David Chiaramonti, per l'opportunità straordinaria di svolgere questa tesi e per la fiducia che mi ha dimostrato.

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Table of Contents

List of Figures

List of Tables

Introduction

Fossil fuels have driven the global economy for over a century, but they are also the main contributors to greenhouse gas emissions, accelerating global warming and causing significant ecosystem degradation. This dependency highlights the urgent need for a new economic model based on renewable resources and reduced carbon emissions. Recent energy crises have underscored the challenge of balancing energy security, equity, and sustainability, urging countries to accelerate their energy transitions to achieve a sustainable and secure energy system. Policies play a crucial role in this transition by encouraging investments in clean energy, fostering innovation, enhancing energy efficiency, and ensuring equitable distribution of benefits. More than 60 countries are currently implementing or formulating decarbonization plans involving alternative fuels like biofuels, hydrogen, and synthetic fuels. These efforts are motivated by global commitments to net-zero emissions, as outlined in the Paris Agreement and aligned with the United Nations Sustainable Development Goals (SDGs)[1]. Decarbonization strategies often target the so-called 'hard to abate' sectors, such as heavy industry, aviation, road, and maritime transport[2]. The European Union (EU) leads these efforts with frameworks such as the Renewable Energy Directive (RED I and RED II), establishing ambitious targets for renewable energy use, including biofuels in transportation. Similarly, the United States, through the Renewable Fuel Standard (RFS), promotes alternative fuels for road transport and, increasingly, for aviation [3]. In this context, the bioeconomy emerges as a strategic pillar, relying on the sustainable use of renewable biological resources to produce energy, chemicals, materials, and food, with a focus on waste reduction and efficiency throughout the value chain [4]. This approach supports a circular economy model, promoting advanced biofuels that reduce dependence on fossil fuels and utilize agricultural waste and non-food resources [5]. Many countries, particularly emerging markets, are developing their own policies to achieve sustainable goals, with biofuels serving as a crucial bridge in the transition to cleaner energy. However, progress is uneven. While some countries in Europe and North America have advanced with strong policies and infrastructure for biofuels and alternative fuels, others are still in the early stages of adopting such frameworks. International cooperation and support for developing economies, such as those in Africa and Southeast Asia, are essential to advancing clean energy transitions globally[6]. Among sub-Saharan countries, Kenya has shown significant interest in developing its biofuel sector. Despite facing challenges such as limited infrastructure, regulatory barriers, and financial constraints, the country has strong potential for biofuel production from diverse feedstocks. Currently, bioethanol is primarily produced from sugarcane, with additional possibilities for crops like sweet sorghum and cassava. Interest is also growing in biodiesel production from feedstocks such as castor oil, sunflower, and Croton megalocarpus, which grows abundantly on marginal lands unsuitable for arable farming, making it an ideal non-edible oil source for biodiesel production [7]. This strategy not only contributes to reducing emissions but also promotes local economic development. The integration of *Croton* oil and Waste Cooking Oil (WCO) as feedstocks in biodiesel production provides Kenya with an opportunity to improve energy security by reducing dependence on fossil fuel imports. Utilizing these local resources minimizes the need for agricultural land to be dedicated to energy crops, thereby preserving biodiversity and mitigating the negative impacts of land use. Furthermore, converting WCO into biodiesel reduces environmental waste producing a low-impact fuel, creating economic opportunities in urban areas through organized collection systems and contributing to environmental sustainability [8]. This study aims to characterize these feedstocks to assess their suitability for biodiesel production, identifying critical aspects and potential challenges that need to be addressed to foster a sustainable biofuel industry. Such initiatives would enhance Kenya's energy self-sufficiency and promote an inclusive development model benefiting both rural and urban communities. Establishing a biofuel supply chain rooted in local resources is a crucial step towards decarbonization and could serve as a model for other countries in the region.

1. Global context and state of the art

In recent decades, both Europe and the United States have developed comprehensive policies to promote biofuels as part of their decarbonization strategies. In Europe, the Renewable Energy Directive (RED) and its update, RED II, set ambitious targets, including achieving 14% renewable energy use in transport by 2030, with a focus on advanced biofuels derived from non-food raw materials like agricultural waste and used oils[3][9]. These directives include strict criteria for greenhouse gas emission reductions and sustainable land use [10]. In the United States, the Renewable Fuel Standard (RFS), established in 2005 and expanded by the Energy Independence and Security Act of 2007, mandates the incorporation of renewable fuels, including ethanol and biodiesel, into the national fuel supply. The RFS sets annual targets for different biofuel categories, including advanced biofuels and biomass-based diesel, based on factors like feedstock availability [11]. It also emphasizes sustainability, requiring a minimum 50% reduction in greenhouse gas emissions compared to conventional fuels. Both regions prioritize the development of advanced biofuels derived from non-food feedstocks to avoid competition with food production. Europe has limited first-generation biofuels and incentivizes advanced biofuels through RED II [12]. The U.S. RFS has created separate markets for advanced biofuels, encouraging innovation in converting lignocellulosic biomass and waste into biofuels [13]. Europe has introduced a sustainability certification system to ensure compliance with stringent environmental standards [14], while the U.S. uses the Renewable Identification Number (RIN) credit system to promote sustainable biofuel production [15]. Public funding and collaboration between the private sector and research institutions have advanced biofuel technologies in both regions, improving the efficiency and sustainability of biofuel production. These policies have positioned Europe and the U.S. as leaders in the global transition towards a low-carbon economy.

1.1 European regulatory framework

The Renewable Energy Directive (RED) differentiates between two main categories of liquid bio-based fuels: **biofuels**, intended for the transport sector, and **bioliquids**, used for energy production and other purposes. Biofuels are further classified into two main groups based on their origin and environmental impact:

- **Conventional Biofuels**: These are derived from food crops such as corn, sugarcane, and vegetable oils (e.g., rapeseed and soybean). Conventional biofuels include bioethanol, produced from sugar and starch crops, and biodiesel, derived from vegetable oils or animal fats. However, their production often competes with food supply, raising food security concerns, particularly in developing countries [3].

- **Advanced Biofuels**: Produced from non-food feedstocks like waste, algae, and agricultural residues, advanced biofuels are considered more environmentally sustainable. The Renewable Energy Directive II (RED II) specifically promotes their use, requiring a minimum percentage of advanced biofuels in transport fuels by 2030. These biofuels are derived from materials listed in Part A of Annex IX of the directive, which focuses on feedstocks with lower environmental impacts [3].

After classifying them based on terminology, the following section aims to delve into the regulatory framework surrounding biofuels in Europe.

Renewable Energy Directive I (RED I - 2009/28/EC) Adopted in 2009, RED I set ambitious goals to increase the use of renewable energy in the EU, mandating that 20% of total energy consumption and at least 10% of transport energy come from renewable sources by 2020. The directive limited the contribution of conventional biofuels due to their competition with food production and established sustainability criteria, requiring biofuels to reduce GHG emissions by at least 35%, later increased to 50% by 2017 and 60% for new installations starting production from 2018. It also prohibited the sourcing of biofuels from areas with high biodiversity value or high carbon stock, such as primary forests, wetlands, and peatlands, to avoid negative environmental impacts.

Renewable Energy Directive II (RED II - 2018/2001/EU) RED II, adopted in 2018, revised the regulatory framework for the period 2021-2030, setting a more ambitious target of 32% renewable energy in the EU's overall consumption by 2030. It particularly emphasizes advanced biofuels, requiring member states to incrementally increase their share in transport fuels from 0.2% in 2022 to at least 3.5% by 2030. The directive also caps the contribution of conventional biofuels to a maximum of 7% of transport energy, preventing extensive use of food-based biofuels. Additionally, RED II introduced a double-counting mechanism, where advanced biofuels count twice towards renewable energy targets, and set a minimum GHG reduction of 65% for new biofuel plants operational from 2021 onwards.

Indirect Land Use Change (ILUC) Directive - 2015 The ILUC Directive (2015/1513) was introduced to address the impact of biofuel production on land use, particularly the risk of converting forests, wetlands, or peatlands into biofuel production areas, which could negate the carbon savings achieved by using biofuels. It limited the contribution of food-based biofuels to 7% of transport energy consumption by 2020 and encouraged the use of biofuels from waste and residues [16].

ReFuelEU Aviation and FuelEU Maritime These initiatives, part of the EU Green Deal, aim to decarbonize the aviation and maritime sectors, which are challenging to electrify. ReFuelEU Aviation sets mandates for the use of Sustainable Aviation Fuels (SAF), aligning with RED II targets, while FuelEU Maritime promotes the adoption of sustainable biofuels for maritime transport. These efforts are crucial for reducing emissions in sectors where alternative solutions are limited.

Certification and Sustainability Requirements The EU mandates that biofuels meet strict sustainability criteria, verified through voluntary certification schemes approved by the European Commission, such as the International Sustainability and Carbon Certification (ISCC) and the Roundtable on Sustainable Biomaterials (RSB). These schemes ensure that biofuels do not contribute to deforestation, biodiversity loss, or social issues [14].

1.2 U.S. regulations on biofuels

The **Renewable Fuel Standard (RFS)**, managed by the Environmental Protection Agency (EPA), is the cornerstone of U.S. biofuel policy. It mandates the blending of biofuels into the national gasoline and diesel supply, setting annual targets for various categories of biofuels:

- **Conventional biofuels**: Primarily corn ethanol, required to reduce greenhouse gas (GHG) emissions by at least 20% compared to conventional gasoline.
- **Advanced biofuels**: Including biodiesel and cellulosic biofuels, achieving a 50% reduction in GHG emissions.
- **Cellulosic biofuels**: Derived from non-food sources like agricultural residues and wood chips, with a required 60% GHG reduction.
- **Biomass-based diesel**: Produced from renewable feedstocks like vegetable oils and animal fats, also meeting the 50% GHG reduction target.

The **Energy Independence and Security Act (EISA)** of 2007 expanded the RFS program, increasing the biofuel blending mandate to 36 billion gallons by 2022, with a strong focus on second-generation biofuels such as cellulosic ethanol. It introduced stricter sustainability criteria to prevent indirect land-use change (ILUC), addressing similar concerns raised in Europe regarding biofuels derived from food crops[17]. Sustainability requirements play a key role in the U.S. biofuel framework. Biofuels must demonstrate specific GHG reductions compared to petroleum-based fuels and adhere to land-use regulations to prevent the conversion of environmentally sensitive areas such as forests and wetlands for biofuel production. The RFS includes a credit trading system known as **Renewable Identification Numbers (RINs)**, which allows refiners to trade or purchase credits to meet their Renewable Volume Obligations (RVOs). This system provides flexibility and helps mitigate risks related to fluctuations in biofuel production capacity. The U.S. biofuel policy has long emphasized the production of **corn ethanol** due to the country's abundant corn supply. While there is a gradual shift towards advanced biofuels, corn ethanol remains a significant component of the RFS.

To support the development of advanced biofuels, the U.S. government has implemented various programs, including:

- **Research and Development Funding**: Provided by the Department of Energy (DOE) and the U.S. Department of Agriculture (USDA) for improving biofuel technologies, particularly for cellulosic ethanol and algae-based fuels.
- **Incentives**: The Blender's Tax Credit (BTC) offers financial support to fuel blenders incorporating biodiesel or renewable diesel. Additionally, loan guarantees from the USDA and DOE assist in building or retrofitting biofuel production facilities[18].

The growth of **Sustainable Aviation Fuels (SAF)** is another key focus, expanding beyond road transport. The Federal Aviation Administration (FAA) and the Department of Defense (DoD) are actively working with the private sector to develop SAF markets and meet aviation decarbonization goals [19].

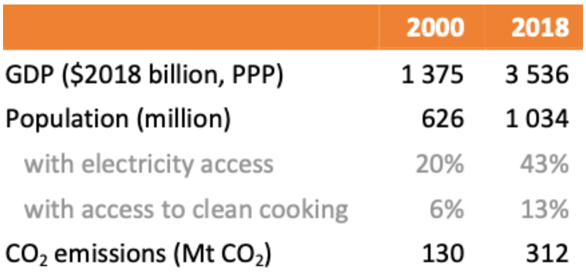
Despite these initiatives, the RFS has faced challenges, such as delays in the commercialization of advanced biofuels and political debates over waiver provisions for small refineries. The future emphasis will be on non-food feedstock biofuels to align with climate change mitigation goals and reduce reliance on imported fossil fuels [20].

1.3 Comparison between regulatory frameworks

After reviewing the regulatory frameworks that guide the development of biofuels in Europe and the United States, it is important to compare in more detail how these regulations influence practical applications and strategic priorities in the two regions. A key distinction in the terminology between Europe and the United States lies in the classification of biofuels. In the European context, conventional and advanced biofuels are differentiated based on the feedstock used: conventional biofuels are derived from food crops, while advanced biofuels are produced from non-food feedstocks listed in Annex IX, Part A of RED II. In contrast, the U.S. defines these categories primarily by their greenhouse gas (GHG) reduction potential: conventional biofuels must achieve at least a 20% GHG reduction, while advanced biofuels require a 50% reduction. Advanced biofuels, which are not derived from food crops, are at the center of European focus, with policies promoting the use of agricultural residues, waste, and lignocellulosic materials to reduce the environmental and social impacts associated with biofuel production. This approach reflects Europe's commitment to mitigating land-use risks and avoiding phenomena such as Indirect Land Use Change (ILUC), which can compromise the sustainability of biofuels [21]. In the United States, while the Renewable Fuel Standard (RFS) calls for the growth of advanced biofuels, the focus remains on corn ethanol and biodiesel produced from vegetable oils, due to the historical influence of the agricultural sector and the availability of large tracts of arable land [22]. The classification of biofuels in the U.S. also includes a specific category for biomass-based diesel, which covers biodiesel and renewable diesel, highlighting a different approach compared to Europe, where renewable diesel is gaining importance, but within a more stringent regulatory context and with greater attention to the origin of feedstocks [22]. While Europe is pushing for the adoption of biofuels in hard-to-decarbonize sectors like aviation and maritime transport, in the United States, the integration of biofuels in road transport remains a priority, although interest in Sustainable Aviation Fuels (SAF) is growing. Another significant difference lies in the approach to certification and sustainability. As mentioned earlier, Europe has developed a stringent certification system to ensure that biofuels meet strict environmental criteria. This system requires producers to demonstrate that their biofuels help reduce greenhouse gas emissions and do not compromise biodiversity or soil health. In the United States, sustainability is certainly a component of the RFS, but with greater flexibility, reflecting priorities around energy security and support for domestic agricultural production. In terms of applications, Europe has launched numerous pilot projects and initiatives to integrate advanced biofuels into maritime and aviation transport, sectors that require energy solutions with high energy density and low carbon intensity. The FuelEU Maritime program, for example, aims to reduce greenhouse gas emissions in maritime transport by adopting sustainable fuels [23]. In the United States, the use of biofuels in aviation is gaining momentum through public-private partnerships, such as the CORSIA (Carbon Offsetting and Reduction Scheme for International Aviation) program by ICAO, which encourages the use of SAF to reduce emissions in the aviation sector [24]. However, regulatory support for road transport remains predominant, with a solid infrastructure for integrating ethanol and biodiesel into traditional fuels [25]. In terms of research and development, Europe focuses more on innovation in advanced biofuels, exploring new technologies for converting and valorizing agricultural residues, while in the United States, the emphasis is on increasing the production and profitability of first-generation biofuels, along with the development of new technologies for advanced biofuels [23]. This comparison highlights how Europe and the United States are following parallel but distinct paths in the promotion and regulation of biofuels. While Europe focuses on strict sustainability and innovation in advanced biofuels, the United States maintains a strong connection with traditional crops while also supporting the development of advanced technologies. This difference in priorities reflects not only the different geographic and agricultural conditions but also a distinct political and strategic vision for the role of biofuels in the energy transition.

1.4 East African Community & Kenya

As a member of the East African Community, Kenya is experiencing a significant energy transition, driven by its rapidly growing population and limited energy infrastructure. The EAC, comprising Kenya, Tanzania, Uganda, Rwanda, Burundi, and South Sudan, aims to promote economic integration and cooperation in sectors such as trade, agriculture, infrastructure, and energy. With a population of approximately 177 million as of 2020, the EAC represents a significant regional market [26].



	2000	2018
GDP ($2018 billion, PPP)	1 375	3 536
Population (million)	626	1 034
with electricity access	20%	43%
with access to clean cooking	6%	13%
CO_2 emissions (Mt CO_2)	130	312

Figure 1 - EAC key indicators [*Africa Energy Outlook (IEA)*]

Despite challenges posed by the global pandemic, the EAC economies have shown resilient growth, with Kenya, Tanzania, and Uganda being the fastest growing in the region, averaging GDP growth rates between 3-6%. Before the pandemic, Kenya led with a growth rate of 5.7% [27]. Agriculture remains the dominant sector, employing over 60% of the EAC's population and contributing nearly 30% to the GDP. However, the services sector, particularly finance and telecommunications, is gaining importance, especially in Kenya [28]. With one of the fastest-growing populations globally, the EAC is experiencing rising energy demand, particularly in urban areas.

Kenya’s population growth rate is 2.2% annually, and urbanization is increasing at 4.2% per year, suggesting a significant surge in future energy requirements [29].

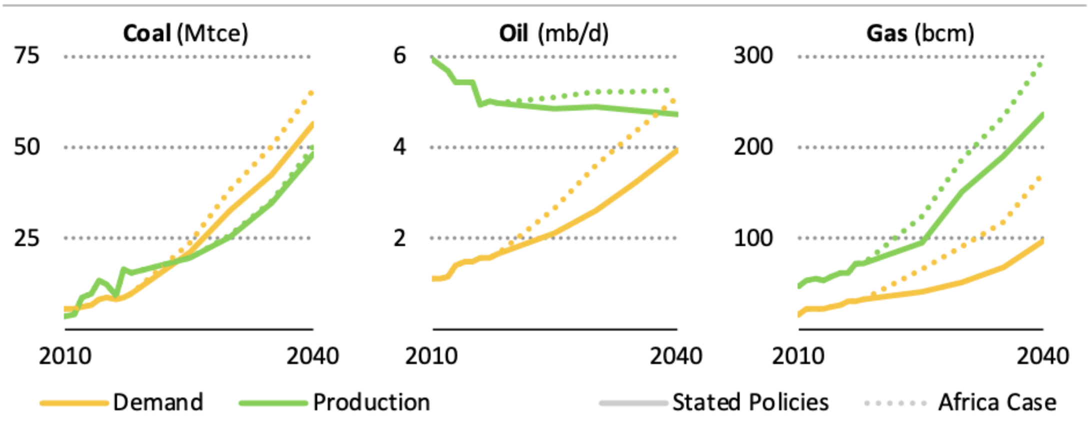
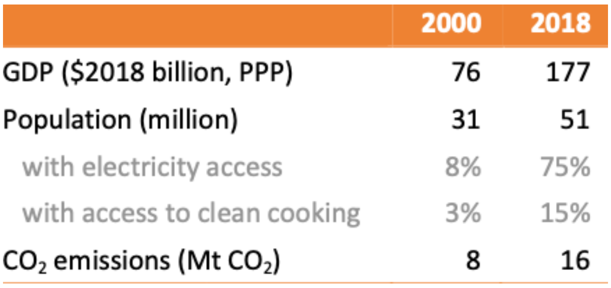


Figure 2 - EAC fossil fuel demand [*Africa Energy Outlook (IEA)*]

Kenya’s relatively stronger economy and strategic geographic position make it a pivotal player in the EAC, serving as a hub for economic activities and policy initiatives. Understanding Kenya's role and regional dynamics within the EAC is crucial for assessing its potential in developing a sustainable biofuel industry to address its energy challenges [30].

1.4.1 Kenya socioeconomic context

Over the past 20 years, Kenya has transitioned from a nation marked by poverty and political instability to one of the leading economies in Sub-Saharan Africa. It is classified as an emerging market with a primarily market-driven economy and some state-owned enterprises. Recently, Kenya surpassed Angola to become the third-largest economy in Sub-Saharan Africa, following Nigeria and South Africa. Geographically, its extensive coastline along the Indian Ocean provides strategic advantages, and its economic prominence in East Africa has made it a regional powerhouse. Kenya is recognized globally for its innovation and rapidly expanding technology ecosystem. With a population of around 57 million, over 80% of whom are under 35, Kenya benefits from a young, educated, and tech-savvy populace, supported by one of Africa's best internet infrastructures. This demographic advantage positions Kenya for rapid economic growth and development [31].



	2000	2018
GDP ($2018 billion, PPP)	76	177
Population (million)	31	51
with electricity access	8%	75%
with access to clean cooking	3%	15%
CO_2 emissions (Mt CO_2)	8	16

Figure 3 - Kenya key indicators [*Africa Energy Outlook (IEA)*]

The country is also a leader in clean energy, with over 90% of its on-grid electricity generated from renewable sources. Kenya has vast geothermal potential, capable of producing 10,000 megawatts, which is more than ten times its current output, making it an attractive destination for companies aiming to boost their green credentials. However, economic growth in Kenya has not been evenly distributed. While GDP per capita grew by an average of 1.8% annually between 2000 and 2022, this growth has been uneven across regions, with some areas experiencing negative growth and others exceeding 4% [32]. Moreover, issues such as corruption and ineffective rule of law remain significant challenges. In the 2022 Corruption Perception Index by Transparency International, Kenya ranked 123rd out of 180 countries, and in the 2023 Index of Economic Freedom, it ranked 135th out of 176. Additionally, Kenya's debt-to-GDP ratio increased from 63% in 2020 to 67.3% in 2022, raising concerns about fiscal stability and debt sustainability due to increased borrowing for public investments [33]. Despite these challenges, there is optimism for Kenya’s future, particularly among the youth. Education and healthcare are seen as public priorities, and sustaining the progress made since 2000 is crucial for Kenya to continue its path toward achieving upper-middle-income status [34].

1.4.2 Kenya's Energy Mix

Kenya is the largest economy in the East African Community (EAC), supported by a diverse economic structure that includes agriculture, manufacturing, tourism, and services. However, energy remains a crucial factor for sustainable growth. Currently, 73% of Kenya’s national electricity supply comes from renewable sources. Geothermal energy is a significant contributor, making Kenya the largest producer in Africa with over 700 MW generated from the Rift Valley.

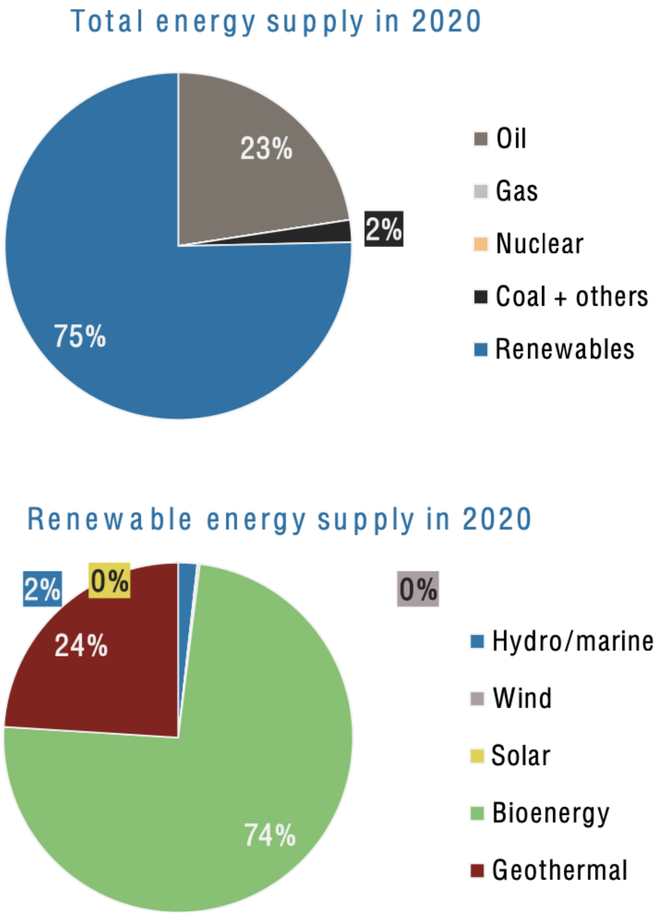


Figure 4 - Kenya energy mix [IRENA]

While hydropower has traditionally been important, it faces reliability issues due to climate variability. The rapid expansion of solar and wind energy, highlighted by projects like the Lake Turkana Wind Power Project, is further diversifying Kenya's energy portfolio. Despite progress in renewables, Kenya remains highly dependent on imported petroleum products, which supply most of the energy for transportation, industrial power, and off-grid needs. The transport sector alone consumes 76% of petroleum products, making it a major source of carbon emissions and underlining the urgent need for cleaner alternatives.

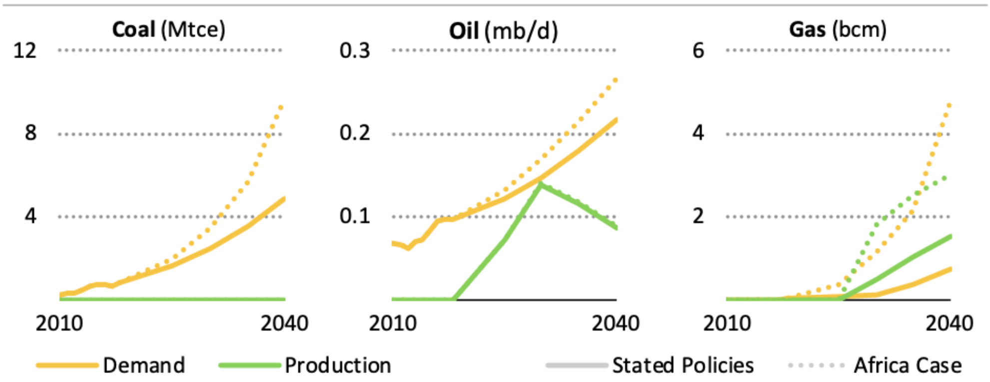


Figure 5 - Kenya fossil fuel demand [*Africa Energy Outlook (IEA)*]

Developing domestic biofuels, such as biodiesel from Croton megalocarpus and Waste Cooking Oil (WCO), could reduce this dependency and improve energy security [35]. Moreover, integrating biofuels into the energy mix would help lower greenhouse gas emissions, supporting Kenya's commitments to international climate agreements like the Paris Agreement [36]. Biofuels offer additional social and economic benefits. Cultivating Croton megalocarpus, which thrives on marginal lands, can help revitalize these areas while providing income for rural communities. Similarly, valorizing WCO addresses urban waste management challenges and generates employment opportunities along the biofuel supply chain. Beyond transportation, biofuels can support rural electrification and off-grid energy solutions, improving energy access in remote areas [37]. The Kenyan government has recognized the potential of biofuels in the "Kenya National Energy Policy," which seeks to integrate renewable energy sources into the national energy matrix, reduce emissions, and stimulate rural economies through the biodiesel value chain. This policy highlights the suitability of Kenya's agricultural conditions and the availability of waste oils and residues for biodiesel production [38]. Kenya is also engaging in international cooperation and seeking climate finance to advance the development of biofuels and promote technological innovation in the energy sector [39]. Industrial initiatives aimed at improving energy efficiency and incorporating biofuels into production processes, particularly in the agro-industrial and transport sectors, could further reduce dependence on fossil fuels and enhance Kenya’s competitiveness. Additionally, exporting biofuels to regional and international markets is being considered to meet the growing demand for sustainable fuels [7], [40]. Despite these advancements, challenges remain, such as the need for adequate infrastructure for collecting and processing biofuel feedstocks and stronger policies to encourage private investment in the sector. Collaboration between the government, private sector, and local communities will be essential to overcoming these barriers and fully realizing the potential of biofuels to meet Kenya's energy needs and those of sub-Saharan Africa [41].

1.4.3 Kenyan regulatory framework

Kenya's National Climate Change Action Plan (NCCAP) 2018-2022 outlines a strategy for addressing climate change through adaptation and mitigation measures.

Adaptation Strategies focus on building climate resilience in sectors such as agriculture, water management, and disaster risk response. This includes promoting climate-smart agriculture, improving water resource management, and strengthening disaster risk management to address floods and droughts [42].

Mitigation Efforts aim to reduce greenhouse gas (GHG) emissions by expanding renewable energy sources like geothermal, solar, and wind, while promoting energy efficiency in transport and industry. The plan also supports sustainable transport options, such as electric vehicles and biofuels, and emphasizes forest conservation and afforestation to enhance carbon sinks [43].

Climate Finance and Investment highlights the need for substantial financial resources, advocating for domestic and international climate finance and encouraging public-private partnerships to support climate initiatives [39].

Governance and Institutional Framework emphasizes coordinated governance between national and county governments, capacity building, and the establishment of a climate change secretariat to align national actions with international agreements like the Paris Agreement.

Monitoring and Reporting Mechanisms include frameworks for tracking progress and improving national GHG inventories to ensure that climate policies are effectively implemented [44].

Capacity Building, Education, and Public Awareness stress the importance of raising climate awareness and building capacity at all levels, from government officials to communities and farmers [45].

Priority Sectors identified for targeted climate action include energy, agriculture, water, forestry, health, and transport, each with specific strategies to reduce emissions and enhance resilience [42].

Biofuels are included in the NCCAP as a key strategy to reduce transport-related emissions and enhance energy security by decreasing reliance on imported petroleum products. The plan advocates for the use of local feedstocks like Croton megalocarpus, agricultural waste, and non-food crops to increase biofuel production [46].

The National Energy and Petroleum Policy (2018) and the Energy Act (2019) are integral to Kenya's energy governance framework. These policies focus on improving energy access, promoting local resource development, and supporting renewable energy adoption. The Energy Act established key institutions like the Energy and Petroleum Regulatory Authority (EPRA) and the Rural Electrification and Renewable Energy Corporation (REREC), which oversee the regulation and promotion of renewable energy, including biofuels. The Kenya Bioenergy Strategy 2020-2027 further supports the development of biofuels by promoting sustainable biomass utilization, clean cooking technologies, and waste-to-energy initiatives. It emphasizes the use of non-food feedstocks such as Croton and agricultural residues for bioethanol and biodiesel production, aiming to reduce dependence on fossil fuels and support a circular economy. Other relevant initiatives include TRACS (Advancing Transport Climate Strategies), which focuses on promoting low-carbon transport fuels in East Africa, aligning with Kenya's goals for sustainable transport outlined in the NCCAP. BioInnovate Africa supports the development of bio-based innovations across the region, providing funding for projects that convert agricultural waste into biofuels. The EAC Regional Bioeconomy Strategy aims to foster sustainable development among East African Community member states by leveraging local resources for energy production and supporting the transition to renewable energy sources. These initiatives complement Kenya's efforts by encouraging the adoption of biofuels and sustainable practices at both national and regional levels. Despite these initiatives, Kenya still lacks a detailed regulatory framework for biofuel production like the EU's RED II or the U.S. Renewable Fuel Standard. There is a need for more specific policies to guide biofuel production and blending standards, alongside continued support for research and private sector involvement to enhance biofuel capacity[41].

2. Vegetable Oils and Their Role in Sustainable Energy Production

In the bioenergy sector, biomass is classified into different types based on its source and potential applications. Energy crops, a specific category of biomass, are cultivated primarily for energy production and are optimized for high energy content and conversion efficiency. These energy crops can be broadly divided into three main groups:

Lignocellulosic Biomass includes materials such as wood, agricultural residues, and grasses. Characterized by a complex structure of cellulose, hemicellulose, and lignin, lignocellulosic biomass requires advanced pretreatment processes to be converted into bioenergy products like cellulosic ethanol, bio-oil through pyrolysis, and solid fuels for combustion. Its abundance and the use of non-food crops make it a sustainable option for bioenergy production, with significant potential to reduce reliance on food-based biofuel feedstocks[47].

Sugar and Starch Crops like sugarcane, corn, and sugar beet are rich in carbohydrates and are primarily used to produce bioethanol through fermentation. This well-established process plays a major role in the biofuel market, particularly in countries like Brazil and the United States, where large-scale production supports the transportation sector[48][49].

Oleaginous Crops, including soybean, sunflower, palm oil, and rapeseed, are notable for their high oil yield.

Oleaginous crops play a pivotal role in bioenergy production due to their flexibility in utilization. The vegetable oils extracted from these crops can be used directly as fuels (PVO) or converted into biofuels like biodiesel and HVO, making them a crucial component in the bioenergy sector[47]. Beyond energy production, these crops contribute to other value chains, with by-products such as protein-rich cake and flour used as animal feed, enhancing both the economic viability and sustainability of oleaginous crops.

This chapter will explore the composition and properties of vegetable oils, their potential for direct use as PVO, and review the various oleaginous feedstocks commonly used in bioenergy applications. It will also discuss the biofuels derived from these feedstocks, such as biodiesel and HVO/HEFA, providing a comprehensive understanding of their role and potential in the energy industry.

2.1 VO characteristics

Vegetable oils are one of the most significant renewable resources for bioenergy production, primarily due to their high energy density and chemical properties. These oils are mainly composed of triglycerides, molecules consisting of a glycerol backbone bound to three fatty acids.

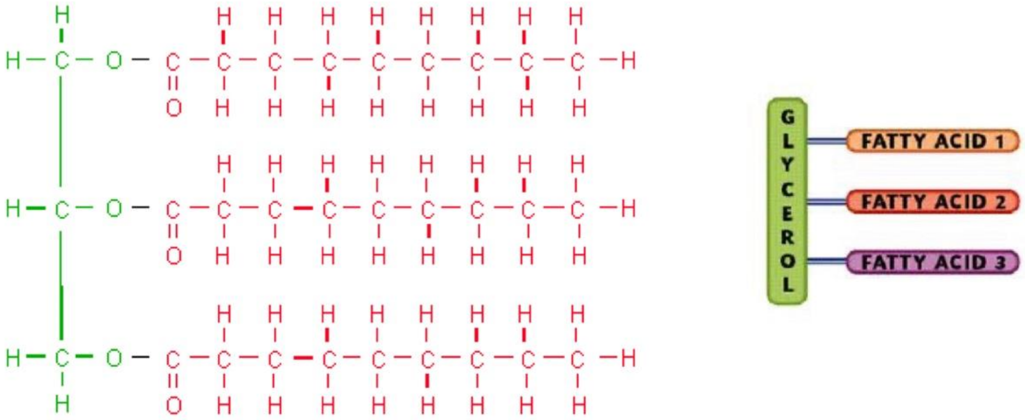


Figure 6 - triglyceride structure

The characteristics of these fatty acids, such as their saturation level and chain length, significantly influence the oil's physical and chemical properties, affecting its suitability as a fuel or a biofuel feedstock [50].

The saturation level of fatty acids is another critical factor. Saturated fatty acids, like stearic and palmitic acid, lack double bonds in their carbon chains, making the oil more stable but also more prone to solidification at room temperature. This results in higher viscosity and poorer cold flow properties, which can be a disadvantage in colder climates. Conversely, unsaturated fatty acids, including monounsaturated fatty acids such as oleic acid, and polyunsaturated fatty acids like linoleic acid, keep oils fluid at lower temperatures, enhancing their suitability for biodiesel production in colder regions. Oils rich in unsaturated fatty acids, such as rapeseed and sunflower oil, demonstrate better low-temperature performance, whereas those with high saturated fatty acid content are more likely to crystallize and exhibit increased viscosity at lower temperatures[50].

Beyond triglycerides, vegetable oils can also contain other minor components such as phospholipids, waxes, and various impurities that can influence the oil's physical and chemical properties as well as its usability as a fuel. The presence and proportion of these components can impact key characteristics such as viscosity, oxidative stability, and combustion properties.

The extraction method significantly affects the quality of vegetable oils. Mechanical extraction, which involves pressing oilseeds or fruits, is a more sustainable and simpler process compared to chemical extraction but generally yields less oil. This process, often preferred for small-scale or decentralized operations, includes cleaning, crushing, pressing, and filtering the seeds. Chemical extraction, on the other hand, utilizes solvents like hexane to obtain higher yields and is more efficient for large-scale production. However, it requires additional refining steps to remove solvent residues, potentially impacting the quality and safety of the final product [51].

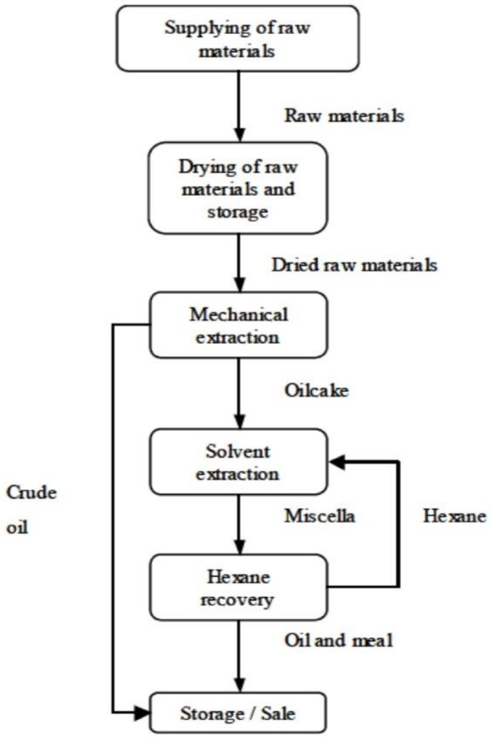


Figure 7 - oil extraction

Both these methods produce by-products like protein cake, a valuable commodity used as a protein source in animal feed due to its high nutritional value. This cake also possesses energy potential due to high calorific value and low moisture content. Despite these advantages, although its high ash content may limit its use as a fuel [52]. Understanding the chemical composition and production methods of vegetable oils is essential to evaluate their potential uses, whether as fuels in their pure form or as feedstocks for biofuels such as biodiesel and HVO. Equally important are their physical properties, which play a critical role in determining their suitability for these applications. The viscosity of vegetable oils, for instance, is typically higher than that of conventional diesel, which can complicate their direct use as Pure Vegetable Oil (PVO) without modifications to the engine or pre-treatment to lower viscosity[53]. Additionally, their oxidative stability varies based on the fatty acid composition, with oils high in polyunsaturated fats being more prone to oxidation, potentially affecting the storage and quality of the resulting biofuel. Cold flow properties, such as cloud and pour points, are also crucial, especially in colder climates where oils rich in saturated fatty acids may solidify, necessitating the use of additives or blending with other fuels to maintain fluidity and performance[50].

2.2 Oleaginous feedstocks

The primary oil crops nowadays are soybean, sunflower, palm, and rapeseed[54]. These crops are cultivated extensively due to their high oil yield and established agricultural practices. However, the reliance on these traditional feedstocks raises concerns regarding food security, land use, and environmental sustainability[55].

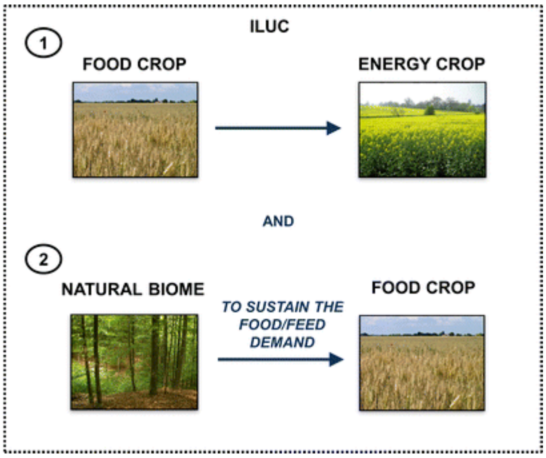


Figure 8 - Indirect Land Usage Change

To address these challenges, there is an increasing interest in alternative feedstocks that do not compete with the food market, such as non-edible oil crops. For example, in Europe, there is growing interest in Camelina (Camelina sativa) due to its low input requirements and its ability to grow on non-arable land[56]. It is considered a promising source of oil for biodiesel production and is currently being studied in temperate regions for its potential to provide a sustainable, non-food-based feedstock[57]. In contrast, in tropical and subtropical regions such as the sub-Saharan area, which is the focus of this research, non-edible oil crops like Croton megalocarpus, Jatropha (Jatropha curcas), and Castor oil (Ricinus communis) are more prominent. These crops are well-adapted to harsher conditions and degraded soils, making them suitable for vegetable oil production without competing with food resources. Specifically, Croton megalocarpus is endemic to East Africa and thrives on marginal lands with minimal agricultural inputs, offering a sustainable option for biofuel production while supporting local economies and land restoration efforts[58]. Additionally, waste-derived feedstocks such as waste cooking oils (WCO) and waste animal fats are gaining traction as cost-effective and environmentally friendly alternatives[59]. Therefore, the selection of feedstocks is critical for the overall sustainability and efficiency of fuel production, influencing not only the environmental impact but also the economic viability of renewable energy solutions.

2.2.1 Edible Feedstocks

Edible feedstocks are the most used for biodiesel production due to their established cultivation practices and high oil yields. However, their use in biofuels raises significant concerns regarding food security and land-use competition.

Rapeseed (Brassica napus L.): It is predominantly cultivated in Europe and thrives in temperate climates. It is the primary source of biodiesel in the region due to its high oil yield, which ranges from 0.7 to 3.4 tons per hectare, depending on cultivation practices and environmental conditions. The oil extracted from rapeseed is characterized by a balanced fatty acid profile, making it suitable for biodiesel production. However, the intensive use of nitrogen and phosphate fertilizers in its cultivation raises concerns about soil and water contamination[54], [60].

Sunflower (Helianthus annuus L.): Crop adaptable to both temperate and Mediterranean climates, is valued for its drought resistance and deep root system, which allows it to grow in areas with limited water resources. Its oil yield ranges from 1 to 3 tons per hectare, and it is rich in unsaturated fatty acids, particularly oleic and linoleic acids, which enhance its oxidative stability, making it favorable for biodiesel production. However, the high-water requirement during the flowering phase can limit its sustainability in arid regions[60].

Soybean (Glycine max L.): It is a major feedstock for biodiesel production in the United States, where it benefits from extensive agricultural infrastructure. Although its oil yield is lower compared to other crops, it is supported by a robust market for its protein-rich meal, which is used as animal feed. However, the environmental impact of soybean cultivation is significant, as it often leads to deforestation and high greenhouse gas (GHG) emissions due to the intensive use of fertilizers and land conversion[61].

Palm Oil (Elaeis guineensis): Primarily cultivated in tropical regions of Southeast Asia and parts of Africa, it is one of the most efficient oil crops in terms of yield, with production exceeding 4 tons of oil per hectare. However, its cultivation is associated with severe environmental issues, including deforestation, loss of biodiversity, and significant GHG emissions. Despite these concerns, palm oil remains a key feedstock for biodiesel due to its high oil content and low production costs[54].

2.2.2 Non-Edible Feedstocks

Non-edible feedstocks, which can be grown on marginal lands, present a sustainable alternative to edible crops as they do not compete directly with food production and can utilize otherwise unproductive land[62].

Jatropha (Jatropha curcas): This is a drought-resistant, non-edible oil crop capable of growing on degraded and arid soils. It has been widely promoted as a sustainable source of biodiesel, especially in developing countries. However, its potential has been limited by inconsistent yields and the need for intensive inputs in some areas. When grown in its native habitat or on marginal lands with minimal inputs, Jatropha can contribute to sustainable biofuel production [63].

Castor (Ricinus communis): Castor oil is valued for its high content of ricinoleic acid, which is beneficial for various industrial applications. The plant is relatively drought-resistant and can be cultivated in semi-arid regions. Despite its lower oil yield and the presence of toxic compounds, its cultivation on marginal lands makes it a viable non-food feedstock for biodiesel production [64].

Croton Megalocarpus: This tree is a native species of East Africa; it grows well on marginal lands and is highly drought resistant. It produces seeds with approximately 32% oil content, which can be extracted for biofuel production. The cultivation of Croton has significant socio-economic benefits for rural communities, as it provides additional income to smallholder farmers who collect and sell the seeds. The oil can be used in stationary engines, such as generators and irrigation pumps, and has been evaluated as a potential feedstock for biodiesel production[65]. Its use as a biofuel feedstock does not compete with food production and can contribute to rural development and land restoration efforts in Kenya.

Alternative Feedstock: Waste Cooking Oil (WCO)

Waste Cooking Oil (WCO), also known as Used Cooking Oil (UCO), is a promising alternative to traditional feedstocks. It is derived from the waste products of the food industry, making it a low-cost and environmentally friendly option for biodiesel production. The use of WCO not only reduces waste but also mitigates the environmental impact associated with the disposal of used oils[66]. WCO typically has high free fatty acid content and impurities, necessitating pre-treatment before biodiesel production[67]. However, its utilization offers significant environmental benefits and aligns with the principles of a circular economy.

2.3 Biofuels from oleaginous feedstocks

Vegetable oils have long been recognized for their potential as a renewable energy source. The concept of using these oils directly as fuels in diesel engines dates to the early 20th century, when Rudolf Diesel famously demonstrated the use of peanut oil in his engine at the 1900 Paris Exposition. This early success showcased the viability of vegetable oils as a fuel source, especially in regions with abundant agricultural production. However, utilizing Pure Vegetable Oil (PVO) directly in diesel engines requires specific modifications, such as preheating and adjustments to injection systems, to overcome challenges related to their high viscosity and poor cold flow properties[53]. Conversely, these vegetable oils can be converted into biofuels like biodiesel and Hydrotreated Vegetable Oil (HVO)[52]. This transformation provides a more versatile and efficient pathway for their use in the energy sector, as these biofuels are more compatible with existing fuel infrastructure and meet modern fuel standards more effectively than PVO. In the following sections, we will explore the production processes and advantages of biodiesel and HEFA, highlighting their role in the transition towards a more sustainable energy system.

2.3.1 Biodiesel

According to the American Society for Testing and Materials (ASTM), biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from renewable lipid sources, such as vegetable oils or animal fats[68]. This renewable origin allows for domestic production, contributing to energy security and sustainability.

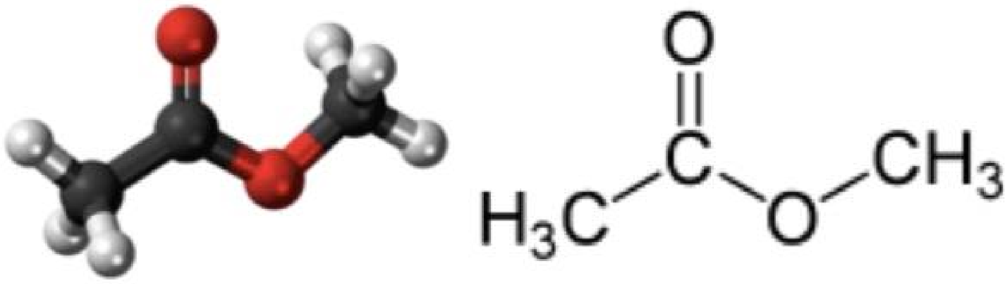


Figure 9 - biodiesel structure

Biodiesel is a renewable fuel produced from vegetable oils or animal fats through a chemical process called transesterification. In this process, triglycerides in the oils react with an alcohol, typically methanol, in the presence of a catalyst to produce fatty acid methyl esters (FAME) and glycerol as a by-product. FAME are the primary components of biodiesel and offer several benefits over conventional diesel, including reduced emissions, higher biodegradability, and a higher flash point[69]. Biodiesel production occurs through transesterification, a chemical reaction between triglycerides (present in oils and fats) and alcohols (usually methanol) in the presence of a catalyst. This process converts the triglycerides into glycerol and fatty acid methyl esters (biodiesel). The reaction can be represented as follows:

Triglyceride (TG)+3Methanol→Glycerol+3Fatty Acid Methyl Esters (FAME)

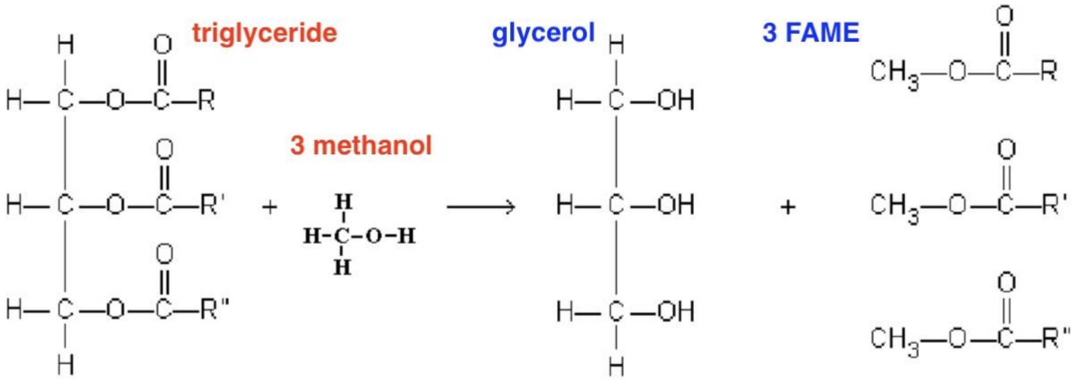


Figure 10 – Transesterification

This reaction typically occurs under mild conditions—between 20°C and 80°C at atmospheric pressure—thanks to the use of alkaline catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). The reaction proceeds through three reversible steps, gradually converting triglycerides into diglycerides, monoglycerides, and finally into glycerol [70]. The final products separate into two distinct phases: biodiesel (upper phase) and glycerol (lower phase), which simplifies the purification process.

Catalysts Used in Transesterification

Three main types of catalysts are used in transesterification: alkaline, acidic, and enzymatic.

Alkaline Catalysts: These are the most used due to their high conversion efficiency under mild conditions and lower corrosiveness. Typical examples include NaOH and KOH. However, these catalysts are sensitive to the free fatty acid (FFA) content in the oil. If the FFA content is high, soap formation can occur, reducing the biodiesel yield. In such cases, a pre-treatment of the oil (pre-esterification or deacidification) is necessary. Alkaline catalysts can be homogeneous (such as NaOH/KOH) or heterogeneous (such as metal oxides or ion exchange resins). Heterogeneous catalysts can be reused and are easier to separate from the product, although they may have limitations depending on the type of feedstock used[71].

Acid Catalysts: Acid catalysts, such as sulfuric acid, are slower than alkaline ones and require higher temperatures and pressures (up to 100°C and 5 bar). However, they are more effective in esterifying free fatty acids (FFA), making them useful for lower quality oils or fats. The main disadvantages include the possibility of forming undesirable by-products, and the reaction must be water-free to maintain efficiency[72].

The mass balance of the transesterification process is generally very efficient, with yields exceeding 97%. For example:

1000 kg of vegetable oil+100 kg of methanol→1000 kg of biodiesel+100 kg of glycerin

One advantage of using methanol in the transesterification process is that biodiesel and glycerin form distinct phases, simplifying the separation and subsequent purification process.

Aspects of Biodiesel Production

Reaction Pressure and Temperature: Although biodiesel production often occurs at atmospheric pressure, some facilities use high-pressure reactors (up to 100 bar) and temperatures up to 250°C. This allows processing feedstocks containing up to 20% FFA without pretreatment, ensuring high-purity glycerin[73].

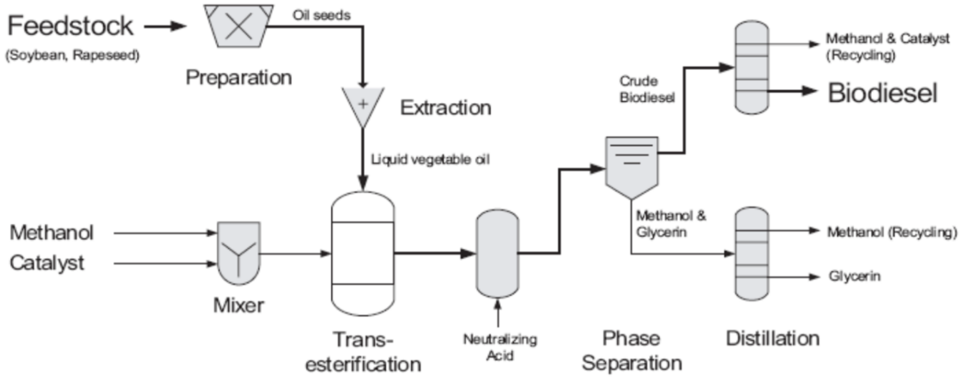


Figure 11 - transesterification process

Batch vs. Continuous Processes: Small-scale production is typically carried out in batches, while larger industrial plants use continuous processes for greater efficiency.

Homogenization of the Reaction Mixture: Since alcohol (such as methanol) is a poor solvent for fats, vigorous mixing or advanced techniques like ultrasonic irradiation or the addition of compatible solvents are necessary to ensure an effective reaction.

Phase Separation: The separation between biodiesel and glycerin can be achieved through centrifugation, the addition of water or extra glycerin, or by cooling the mixture.

Product Purification: After separation, both biodiesel and glycerin must be purified to remove traces of catalysts, soaps, and fatty acids, ensuring that the final product meets the required standards for use in diesel engines or industrial applications[74].

2.3.2 HVO & HEFA

Starting from the same kind of feedstock it's possible to produce another class of biofuels, the so-called drop in fuels, these are hydrocarbons, not oxygenated fuels as biodiesel. Additionally, they are not produced through transesterification, but these require hydrotreatment[75].

Hydrotreated Vegetable Oil (HVO) and Hydroprocessed Esters and Fatty Acids (HEFA) are advanced biofuels produced through the hydrotreatment of renewable lipid sources such as vegetable oils, animal fats, and waste oils[76]. This process involves the catalytic removal of oxygen from the triglycerides and fatty acids in the feedstock, resulting in a high-quality paraffinic hydrocarbon that closely resembles conventional fossil fuels[77].

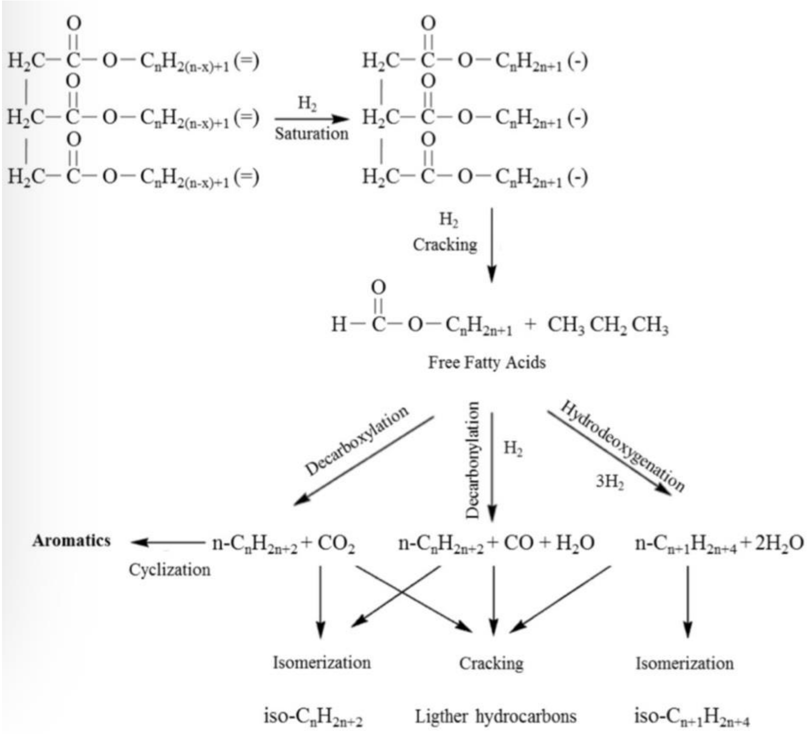


Figure 12 - hydrotreatment

The hydrotreatment process consists of several key steps:

Hydrodeoxygenation is the primary reaction for removing oxygen from the feedstock. It involves breaking the C–O bonds in the fatty acids or triglycerides, converting them into water and hydrocarbon chains. This reaction occurs in the presence of hydrogen and a metal catalyst, such as nickel-molybdenum or cobalt-molybdenum, under high temperatures (300-450°C) and pressures (20-100 bar)[78].

In parallel, **decarbonylation** and **decarboxylation** reactions remove oxygen as carbon monoxide (CO) and carbon dioxide (CO_2), respectively. These reactions result in the loss of one carbon atom from the fatty acid chain, producing shorter hydrocarbon molecules. Decarboxylation is especially useful for treating feedstocks with high free fatty acid content, as it helps convert fatty acids directly into hydrocarbons without the need for full hydrogenation[76].

After hydrotreatment, an additional isomerization step can be included, especially for HEFA production. This step rearranges the hydrocarbon molecules to improve the fuel's cold flow properties, making HEFA suitable for use as a Sustainable Aviation Fuel (SAF). This step is crucial for meeting the stringent low-temperature requirements for aviation fuel as defined by standards such as ASTM D7566[47].

Differences Between HVO and HEFA:

HVO is primarily produced for use as renewable diesel, suitable for blending with or replacing fossil diesel in existing diesel engines. It meets the EN 15940 standard for paraffinic diesel fuels, offering advantages such as high cetane number, absence of sulfur and aromatics, and improved combustion properties. HEFA, on the other hand, is specifically tailored for the aviation industry as a renewable jet fuel. It includes an additional isomerization step to enhance cold flow properties and meet the ASTM D7566 standard for sustainable aviation fuels (SAF)[79]. HEFA's production process is more complex due to the need to meet the stringent requirements for use in jet engines, such as a very low freezing point and high thermal stability[80].

Both HVO and HEFA provide significant environmental benefits compared to conventional fossil fuels. They contribute to reduced greenhouse gas emissions, improved air quality due to lower particulate emissions, and decreased reliance on fossil fuels. They are compatible with existing fuel distribution systems and engines, making them a viable alternative for immediate use in transportation and aviation sectors. In conclusion, while HVO and HEFA share a similar hydrotreatment production pathway, their end-use applications differ due to the additional processing steps required for HEFA to meet aviation fuel standards. Both represent important steps toward sustainable fuel production and contribute to energy security and environmental sustainability.

Technological Approaches for HVO Production: PV + Electrolyzer vs Steam Methane Reforming

Two main approaches can be used to produce the hydrogen needed for oil hydrogenation in HVO production: water electrolysis using renewable energy (PV + Electrolyzer) and Steam Methane Reforming (SMR)[81].

The PV + Electrolyzer approach uses solar energy to power an electrolyzer that splits water into hydrogen and oxygen. This method is highly sustainable since the hydrogen produced is "green" and does not generate CO_2 emissions. However, the technology is currently expensive and requires significant installed solar capacity, which can be limiting in areas with underdeveloped energy infrastructure[82].

In contrast, Steam Methane Reforming is the predominant technology for hydrogen production globally due to its efficiency and relatively low costs. However, this process produces CO_2 as a by-product, contributing to greenhouse gas emissions unless combined with carbon capture and storage (CCS) technologies. In contexts like Kenya, where natural gas availability and SMR technology may be limited, adopting more sustainable technologies like PV + Electrolyzer could be a strategic long-term option despite higher initial costs.

While biodiesel is produced through a relatively simple process, HVO, on the other hand, is produced through a catalytic hydrogenation process, which involves the removal of oxygen from the triglycerides and fatty acids present in vegetable oils or animal fats using hydrogen under pressure. This process requires more sophisticated infrastructure and advanced technology, often available only in large-scale refining facilities.

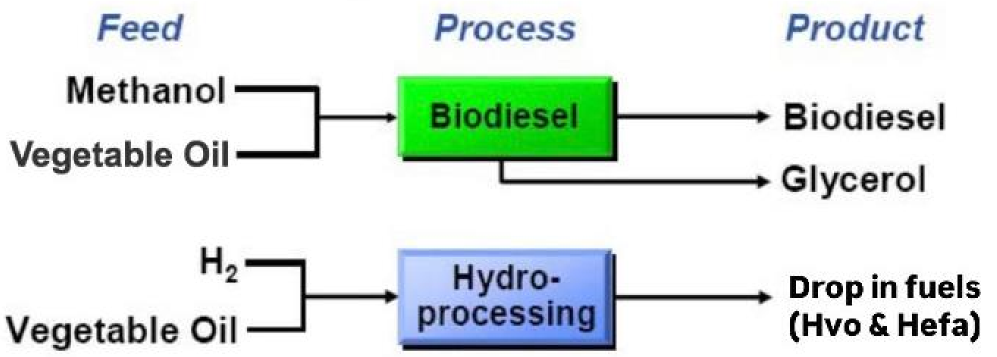


Figure 13 - transesterification vs hydrotreatment

The main advantage of HVO over biodiesel is its chemical composition, which is very similar to that of fossil diesel, making it fully compatible with existing diesel engines without the need for modifications. The applications of HVO extend beyond road transport, including maritime transport and aviation, where fuel density and stability are critical[81].

3. Experimental Methodology for Feedstocks Characterization

In this section, the methodology for evaluating the suitability of Croton megalocarpus oil and waste cooking oil (WCO) as feedstocks for biodiesel production is outlined. Both the chemical composition and properties of the oils were analyzed, as these factors critically influence the reaction conditions for transesterification and the quality of the final biodiesel product[61]. First, GC-MS and FTIR were used to determine the fatty acid distribution and identify functional groups. Following the compositional analysis, titrations were performed to measure the acid value, which reflects the concentration of free fatty acids (FFAs) in the oil[72]. This is a critical parameter, as high FFA levels require pretreatment to avoid soap formation during transesterification, which could hinder the reaction efficiency and biodiesel yield[83]. During the initial acid value test on the first Croton megalocarpus oil sample, a high acid value was recorded, indicating significant degradation of the oil. To assess the extent of degradation, a fresh sample of Croton megalocarpus oil was acquired and analyzed alongside the degraded sample. This allowed for a comparative study to quantify the degradation and assess how it influenced the oil's suitability for biodiesel production. The old sample, with its elevated acid value, provided insights into how long-term storage or poor handling could impact oil quality and biodiesel yield. The main characteristic of interest are physical and chemical properties as Density, Viscosity, Heating value (HHV), Cold temperature behavior. Additionally, the iodine number was measured to provide insight into the degree of unsaturation in the oils, as it influences the oxidative stability of the resulting biodiesel. The peroxide value was assessed to determine the level of oxidation in the oils, which directly affects the fuel's stability and shelf life. The saponification value was calculated to offer information about the average molecular weight of the triglycerides in the oils, aiding in the determination of the appropriate amount of catalyst required for transesterification. Finally, the moisture content was measured because water can interfere with the transesterification reaction, reducing yield and potentially leading to soap formation. However, it was not possible to measure some other critical properties, such as the flash point, cetane number, and other characteristics due to equipment limitations. The samples analyzed in this study consist of *Croton megalocarpus* oil and waste cooking oil (WCO). The *Croton megalocarpus* oil was sourced from **Eco Fuels Kenya (EFK)**, a leading company involved in the collection and processing of croton nuts for biofuel production. EFK operates in collaboration with over 5,000 subsistence farmers across Kenya, primarily in counties such as Nyeri and Nanyuki, where the croton trees are cultivated. These farmers harvest the croton fruits, which are then processed by EFK. The oil extraction involves drying, de-husking, and pressing the croton nuts to extract oil that is later refined for various uses, including biodiesel production[58]. The second sample, **waste cooking oil**

(WCO), was collected from a variety of restaurants and bars across Nairobi. WCO is an increasingly popular feedstock for biodiesel production due to its abundance and low cost, offering a way to recycle used oils while reducing waste. The collected WCO was subjected to filtration to remove large food particles and residues, ensuring a cleaner sample for further analysis. This step is critical because impurities in WCO can interfere with the transesterification process, leading to soap formation or lower biodiesel yields[84]. The choice of these two feedstocks—croton oil and WCO—reflects a balance between exploring a sustainable, locally available resource (*Croton megalocarpus*) and utilizing an already existing waste stream, both of which have significant potential to contribute to Kenya's renewable energy goals.

3.1 GCMS

In this study, GC-MS was critical for analyzing the fatty acid composition of both Croton megalocarpus oil and waste cooking oil (WCO). The triglycerides in these oils were converted into Fatty Acid Methyl Esters (FAME) through a derivatization process to make them suitable for GC-MS analysis [85]. Gas Chromatography-Mass Spectrometry (GC-MS) is a sophisticated analytical method used to separate, identify, and quantify the components of a sample, especially useful for volatile and semi-volatile compounds such as fatty acid methyl esters (FAME) in biodiesel research [86]. GC-MS operates by combining two stages: gas chromatography (GC) and mass spectrometry (MS).

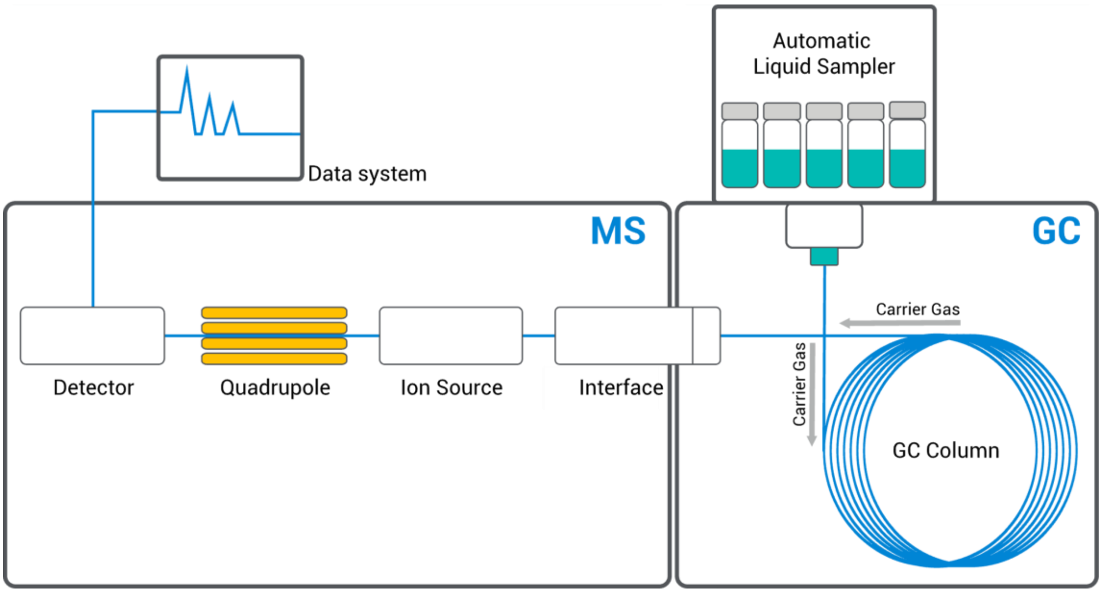


Figure 14 - GCMS general scheme

In the first part, the sample, which must be volatile or derivatized to a volatile form, is injected into the GC system. In this study, oils are converted to FAME via derivatization for this reason. Once injected, the sample is heated and vaporized in a carrier gas. The vaporized sample moves through a long, coiled column, which is coated with a stationary phase. As the sample components pass through the column, they are separated based on their boiling points and interaction with the stationary phase. Compounds with lower boiling points or weaker interactions with the column move faster, while those with higher boiling points or stronger interactions move more slowly. This allows for the separation of individual fatty acid methyl esters. Each compound takes a different amount of time to pass through the column, called its retention time. This time helps in identifying the compound when compared with known standards[86].

In the second part, Once the compounds exit the GC column, they enter the mass spectrometer. Here, the compounds are ionized, through electron impact ionization (EI), which bombards the molecules with high-energy electrons, breaking them into ions which are then separated based on their mass-to-charge ratio (m/z)[87]. Heavier ions travel slower, while lighter ions travel faster, enabling separation within the mass analyzer. Finally, the separated ions hit a detector, generating a signal proportional to their abundance. The resulting data are presented as a mass spectrum, which shows the m/z ratios and their relative intensities. The mass spectrometer provides a mass spectrum for each component, which acts as a "fingerprint" for the compound. By comparing the spectra with known reference spectra, individual compounds can be identified with high precision. This step is essential in determining the specific fatty acids present in the oil samples.

GC-MS measurements were performed setting these parameters:

Column Oven Temperature: The oven temperature was initially set at 60°C and then gradually increased to 250°C at a rate of 10°C per minute, held for 10 minutes to ensure proper volatilization of the sample components. This temperature ramp ensures that lower boiling compounds are eluted first, followed by higher boiling ones, allowing for efficient separation.

Injection Temperature: Set at 200°C to completely vaporize the sample without causing degradation. It ensures the sample enters the column in a gaseous state for effective chromatographic separation.

Injection Mode: A split mode with a 1:10 ratio was used to ensure precision in sample volume handling.

Ionization Temperature: After separation by the GC, the components were introduced into the mass spectrometer, where they were ionized by electron impact at 200°C and detected based on their mass-to-charge ratio (m/z)[85]. This ion source temperature is optimal for ensuring that the FAME molecules are ionized without excessive fragmentation, preserving the integrity of the ions for accurate mass detection.

GC-MS allowed to identify the different fatty acids in the oils and quantifies the relative amounts of each fatty acid present, which is crucial for understanding the balance of saturated and unsaturated fatty acids. Both Croton megalocarpus oil and WCO are complex mixtures of various fatty acids. GC-MS can separate and analyze these mixtures to provide a clear picture of the oil's composition.

3.1.1. Derivatization

Fatty acids in their underivatized form are polar compounds and in their natural form are difficult to volatilize. This represents a problem for gas chromatography, which requires volatile compounds for effective separation. To solve this issue the samples are derivatized into fatty acid methyl esters (FAME), which are non-polar and more volatile, making them suitable for GC-MS analysis[88]. The derivatization process used in this study involves KOH in methanol (KOH-MeOH) as the derivatizing agent, which converts triglycerides into FAME through a transesterification reaction. Additionally, n-Hexane is added to extract the FAME from the reaction mixture, allowing for easy separation of the non-polar FAME from the polar glycerol byproduct. For derivatizing the samples, a small volume (40 µL) of each oil was placed into 10 mL tubes for processing. 3 mL of a potassium hydroxide in methanol (KOH-MeOH) solution was added to the sample, followed by ultrasonication to ensure proper mixing. The mixture was heated at 60°C for 30 minutes to facilitate the conversion of triglycerides into FAME. After heating, the mixture was cooled to room temperature, then 3 mL of n-Hexane was added to create a medium for FAME migration, and 2 mL of distilled water was added to assist in phase separation. Thorough mixing produced a biphasic system where the FAME moved into the hexane layer, while glycerol remained in the aqueous layer. The upper hexane layer containing the FAME was carefully transferred into a clean vial using micropipettes. The solution was dried using a MI-VAC DNA concentrator at 40°C for 10 minutes to remove moisture and hexane, yielding a concentrated FAME sample. The dried FAME was reconstituted with 1.5 mL of n-Hexane, filtered through a 0.22 µm syringe filter, and prepared for GC-MS analysis. This ensures a homogeneous mixture suitable for precise detection.

3.2 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a technique used to obtain the infrared spectrum of a sample. It provides information about the chemical bonds and molecular structure of a substance by measuring how molecules absorb infrared light at different wavelengths[89]. FTIR works on the principle that molecules absorb specific frequencies of infrared light corresponding to the vibrations of their chemical bonds. This technique is essential for identifying the functional groups in organic compounds. Every molecule has unique vibrational modes, which correspond to the movement of its atoms relative to each other, such as stretching, bending, or twisting. These vibrations occur at specific frequencies, depending on the type of bond and the molecular environment. When infrared light passes through a sample, certain wavelengths are absorbed, causing bonds to vibrate. The core of FTIR is an interferometer, which splits a beam of infrared light into two paths using a beam splitter. One path is reflected off a fixed mirror, and the other is reflected off a moving mirror. When these beams recombine, they create an interference pattern, which is characteristic of the light's path difference. As the moving mirror shifts, the interferometer generates a pattern of light intensity over time called an interferogram[90]. This contains information on all wavelengths of light that passed through the sample. The use of the Fourier Transform allows to convert the interferogram (a time-domain signal) into a spectrum (a frequency-domain signal). This spectrum represents the absorption of light at different wavelengths, which corresponds to the vibrational energies of the chemical bonds in the sample. The resulting spectrum displays peaks at specific wavelengths where the sample absorbed infrared light[90]. Each peak corresponds to a specific type of molecular vibration, providing detailed information about the functional groups present in the sample.

The FTIR machine uses KBr plates as the medium for mounting the sample. KBr is chosen because it is transparent to infrared light and chemically inert, meaning it won’t react with the sample or interfere with the measurement. The plates are thoroughly cleaned with acetone to ensure no contamination affects the resulting spectrum. A small amount of the liquid sample (e.g., a drop of Croton megalocarpus oil or WCO) is applied to the KBr plate using a capillary tube, ensuring precise control of the sample amount. The sample is spread into a thin film on the plate to allow infrared light to pass through uniformly, preventing over-absorption. The KBr plate with the sample is mounted into the machine's sample holder, ensuring consistent positioning for analysis. Infrared light is passed through the sample, and the machine detects how much light is absorbed at each wavelength. Different functional groups in the sample absorb infrared light at characteristic wavelengths, which are recorded as peaks in the resulting spectrum. The resulting spectrum is a plot of absorbance vs. wavelength (wavenumber, cm^{-1}), showing which chemical bonds are present based on the specific frequencies at which light is absorbed. The raw data is processed to correct for environmental factors through atmospheric compensation, which accounts for absorption due to gases like CO_2 and H_2O, ensuring that only the sample's absorption is reflected. Additionally, the data undergoes normalization to adjust peak intensities for consistent comparison across different samples, smoothing to reduce noise in the spectrum for easier interpretation, and baseline correction to remove any background interference and set the baseline of the spectrum to zero absorbance. The final corrected spectrum, representing the molecular vibrations of the sample, is obtained, and the peaks are assigned to specific functional groups present in the oil samples[89].

3.3 Density

Density describes the mass of a substance per unit volume, typically expressed in kilograms per cubic meter (kg/m^3). In the context of biodiesel production, it plays a role in fuel handling, injection systems, and overall performance when used in diesel engines. Understanding the density of the oils before conversion to biodiesel provides a baseline for quality control[91].

To measure the density of each oil sample (Croton megalocarpus oil, WCO, and diesel for comparison), begin by thoroughly mixing the samples to ensure homogeneity and eliminate potential errors caused by stratification. Place an empty container on a precision balance and reset the balance to zero. Carefully add 200 mL of the oil sample into the container and record the mass. Repeat this process five times for each sample to obtain reliable and accurate measurements, ensuring that the volume is precisely measured each time to maintain consistency. Record the mass after each trial and note any discrepancies. The density of each sample can then be calculated as the ratio of mass over volume:

$$\rho = \frac{m}{V}$$

After five measurements, the average density is calculated to provide a more accurate value. The same procedure is followed for Croton megalocarpus oil, waste cooking oil, and diesel (used as a reference). Diesel serves as a baseline for comparison since its density is well established.

3.4 Kinematic viscosity

Kinematic viscosity is a critical property in the evaluation of oil feedstocks for biodiesel production. It measures the oil's resistance to flow under the force of gravity and is expressed in centistokes (cSt). The importance of kinematic viscosity lies in its direct impact on the flow characteristics and performance of biodiesel as a fuel and it's a key parameter for pumping and injection systems[92]. Viscosity influences how easily the fuel can be pumped, stored, and filtered[92]. High-viscosity oils might clog filters and fuel lines, especially in cold weather, where they become even thicker. Measuring kinematic viscosity ensures that the oils used will flow correctly under various conditions. Biodiesel standards such as EN 14214 in Europe and ASTM D6751 in the U.S. specify acceptable ranges for the viscosity of biodiesel fuels. Oils used as feedstocks for biodiesel must fall within these ranges after conversion to ensure that the fuel meets quality and performance standards. Viscosity is temperature-dependent; oils tend to become less viscous at higher temperatures, therefore, measuring viscosity at both room temperature and elevated temperatures (e.g., 40°C) provides insights into how the oil will behave under different operating conditions.

The kinematic viscosity of Croton, waste cooking oil (WCO), and diesel was measured using a Redwood Viscometer. The instrument consists of a cylindrical cup with an orifice at the base, through which 50 mL of oil flows into a narrow-neck flask placed below. The flow time, recorded in Redwood seconds using a stopwatch, is then used to calculate the viscosity. Before starting the test, the oil cup and orifice were thoroughly cleaned, and the orifice was closed with a ball valve to prevent premature flow. The procedure began by filling the cup with each oil sample up to the marked level. Diesel was included as a reference. Thermometers were used to monitor the temperatures of the oil and the water bath to maintain the desired conditions. Measurements were first taken at room temperature by opening the ball valve and recording the time it took for the oil to flow into the flask. This process was repeated after heating the water bath to 40°C, ensuring that the oil samples also reached this temperature. The recorded times at both temperatures provided the data required to calculate the kinematic viscosity for each oil sample using the following formula:

$$\nu = At - \frac{B}{t}$$

Where:

- $A=0.26$
- $B=172$
- t=time in Redwood seconds (measured at both room temperature and 40°C).

3.5 Higher heating value

The bomb calorimeter measures the higher heating value (HHV) of a fuel, also known as the gross calorific value. This value represents the total amount of energy released during complete combustion, including the heat recovered from the condensation of water vapor in the combustion products[93]. Therefore, when using a bomb calorimeter, it's possible to obtain the HHV, which accounts for all the energy content of the fuel, making it a comprehensive measure of its energy potential. This is crucial for evaluating fuels like Croton oil and waste cooking oil (WCO) for biodiesel production, as the HHV provides a complete picture of their energy release upon combustion, which is necessary for understanding their performance in energy applications[94].

A bomb calorimeter is used to determine the higher heating value (HHV) of an oil sample by burning it in a sealed, oxygen-rich environment. The heat released from the complete combustion of the sample raises the temperature of the surrounding water, allowing the total energy content to be calculated. To perform this test, a small oil sample, around 0.5 grams, is weighed with high precision and placed into a combustion cup. The cup is positioned inside the bomb calorimeter, and a fuse wire is attached to electrodes, contacting the sample. The bomb is then sealed and filled with pure oxygen at approximately 25 atm to ensure complete combustion.
The Initial temperature of the water bath surrounding the bomb is recorded before ignition. When the electric ignition system triggers the combustion, the oil sample burns completely, and the heat produced raises the temperature of the water bath. After combustion, the final temperature of the water bath is measured. The change in temperature, along with the known heat capacity of the calorimeter system, is used to calculate the calorific value of the oil. This process provides an accurate measurement of the HHV through the following formula:

$$CV = \frac{Heat\ Capacity\ of\ Calorimeter \cdot Temperature\ Change}{Mass\ of\ Sample}$$

3.6 Acid value

The acid value (AV) is a measure of the free fatty acids present in the oil, expressed in milligrams of potassium hydroxide (KOH) required to neutralize the free acids in one gram of oil. It is an important indicator of oil quality, as high acid values suggest the presence of degradation products, which may negatively affect the transesterification process used in biodiesel production[95]. The free fatty acid (FFA) content is closely related to the acid value and represents the percentage of fatty acids in the oil. Elevated FFA levels can lead to soap formation during biodiesel production, reducing the efficiency and yield[96].

For this procedure, two Croton oil samples (degraded and non-degraded) and one sample of waste cooking oil (WCO) were analyzed. Each sample was prepared by weighing 2.5 g and 10 g of oil and dissolving them in 50 mL of ethanol in separate Erlenmeyer flasks. A few drops of phenolphthalein indicator were added to each solution, which initially remained colorless, indicating the presence of unneutralized free fatty acids. The titration was carried out using a 0.1 M potassium hydroxide (KOH) solution. The KOH was gradually dispensed from a burette into the oil-ethanol mixtures while stirring continuously with a magnetic stirrer. The endpoint of the titration, marked by a persistent light pink color for 15-30 seconds, signified complete neutralization of the free fatty acids. The volume of KOH required to reach the endpoint was recorded for each sample and used for calculating the acid value as follows:

$$AV = \frac{V \times M \times 56.1}{m}$$

Where:

- V is the volume of KOH used (in liters)
- M is the molarity of KOH (0.1 M)
- 56.1 is the molecular weight of KOH
- m is the weight of the oil sample (in grams).

3.7 Moisture content

High moisture levels can negatively impact the transesterification process by promoting hydrolysis, which increases the free fatty acid (FFA) content and leads to soap formation[97]. This reaction not only reduces the yield of biodiesel but also complicates the separation of biodiesel and glycerin, making the process less efficient. Moreover, water in the oil can cause corrosion in storage tanks and fuel systems and lower the quality of the final biodiesel product by increasing its risk of microbial contamination and oxidation during storage[97]. Therefore, controlling and minimizing moisture content is crucial for ensuring the efficient conversion of oils into high-quality biodiesel.

The AOCS Ca 2c-25 standard outlines the procedure for determining the moisture and volatile content in oils and fats using the oven drying method. The process begins by accurately weighing approximately 5-10 grams of the oil or fat sample into a pre-weighed crucible. The crucible, containing the sample, is then placed in a drying oven set at 105°C. The sample is dried for 1-2 hours or until it reaches a constant weight, with the drying time depending on the type of oil or fat and its initial moisture content.

After drying, the crucible is removed from the oven and transferred to a desiccator to cool to room temperature, preventing moisture absorption from the air during cooling. Once cooled, the crucible and the dried sample are reweighed.

The moisture content is calculated using the weight difference before and after drying, according to the specified formula in the standard:

$$Moisture\ Content\ (\%) = \frac{mi - mf}{mi} \cdot 100$$

Where mi and mf stand respectively for initial and final mass.

3.8 Iodine value

The iodine value measures the degree of unsaturation in oils and fats, indicating the number of double bonds present in the fatty acid chains[98].
It is a key parameter in assessing the reactivity and stability of oils, as higher iodine values suggest a higher degree of unsaturation. This property is crucial for determining the oil's suitability for biodiesel production and its oxidative stability during storage[99].

The AOCS Cd 1-25 standard is used to determine the iodine value of oils and fats, reflecting their degree of unsaturation. The procedure involves weighing 0.2-0.3 grams of the sample into a 250 ml Erlenmeyer flask, followed by the addition of 20 ml of glacial acetic acid and 25 ml of iodine solution (Hanus or Wijs).

The mixture is then allowed to react in the dark for 30 minutes. After adding 20 ml of potassium iodide and 100 ml of distilled water, the solution is titrated with 0.1 N sodium thiosulfate until a pale-yellow color appears. A starch indicator is added, and titration continues until the blue color disappears. A blank titration is also performed to determine the volume of thiosulfate needed to calculate the iodine value. Iodine value is then calculated as follows:

$$Iodine\ Value = \frac{(B - S) \times N \times 12.69}{Weight\ of\ sample\ (g)}$$

where:

- B = volume of thiosulfate used in the blank (ml)
- S = volume of thiosulfate used in the sample (ml)
- N = normality of thiosulfate solution
- 12.69 = conversion factor to obtain the iodine value

3.9 Pour Point

The pour point is the lowest temperature at which a liquid, such as oil, remains pourable and does not solidify. This is a critical parameter for assessing the performance of fuels and oils in cold conditions, as it indicates their usability and flow characteristics at low temperatures[61]. For biodiesel and petroleum products, a lower pour point is preferable to prevent issues like fuel line blockages in cold climates. The ASTM D97 standard is widely used to measure this property across various types of oils and biodiesel fuels. For instance, biodiesel blends often require additives to lower the pour point and enhance their performance in colder temperatures, ensuring they remain fluid and functional[100].

The procedure for determining the pour point of oil samples was conducted according to the AOCS Cc 11-53 standard. Approximately 45 mL of the oil sample was poured into a clean, dry test jar. The jar was then placed in a cooling bath set at a temperature slightly above the anticipated pour point. Following the standard guidelines, the sample was allowed to cool slowly, and the temperature was monitored at intervals of 3°C using a thermometer. After each interval, the jar was gently tilted to observe the movement of the oil. The lowest temperature at which the oil stopped flowing was recorded as the pour point.

3.10 Peroxide Value

The peroxide value measures the peroxide content in oils, reflecting the degree of primary oxidation. It is expressed in milliequivalents per kilogram (mEq/kg), quantifying the amount of active oxygen in the form of peroxides and hydroperoxides[101]. A milliequivalent (mEq) is the amount of a substance that can react with or supply one millimole of hydrogen ions (H^+) in a chemical reaction. Higher peroxide values indicate more advanced oxidation, suggesting that the oil is degrading and potentially becoming rancid[95].

The AOCS procedure for determining the peroxide value involves the following steps: Weigh approximately 5 grams of oil into a stoppered flask. Add 30 mL of 3.5% hydrochloric acid and 1 mL of saturated potassium iodide solution, mixing well and allowing the reaction to occur in the dark for 1 minute. Next, add 30 mL of distilled water and titrate the mixture with 0.01 N sodium thiosulfate solution until a pale-yellow color is observed. Add a few drops of starch solution as an indicator, then continue titrating until the blue color disappears, indicating the endpoint. The peroxide value can then be calculated using the volume of sodium thiosulfate used in the titration using the following formula:

$$\text{Peroxide value (meq/kg)} = \frac{(VB - VS) \times N \times 1000}{Sample\ Weight}$$

Where:

- VB = volume of sodium thiosulfate used in the blank (ml)
- VS = volume of sodium thiosulfate used in the sample (ml)
- N = normality of the sodium thiosulfate solution.

3.11 Saponification Value

The saponification value is a measure of the amount of potassium hydroxide (KOH) needed to completely saponify one gram of the sample. This value reflects the average molecular weight of the triglycerides present, with higher values indicating smaller molecules that can influence the biodiesel conversion process. Additionally, it provides insight into the quality and composition of the oil, which is essential for evaluating its overall suitability as a biodiesel feedstock[68].

The procedure starts by weighing 2-3 g of oil into a stoppered flask and add 25 ml of 0.5 N potassium hydroxide (KOH) solution in alcohol. Attach a condenser to the flask and heat the mixture in a water bath for 1 hour, shaking occasionally to ensure complete saponification.

After heating, allow the flask to cool. Add a few drops of phenolphthalein indicator, then titrate with 0.5 N hydrochloric acid (HCl) solution until the pink color disappears.

The saponification value can then be calculated based on the volume of HCl used in the titration as follows:

$$Saponification\ value\ (mg\ KOH/g)\ =\ \frac{(VB - VS) \times N \times 56.1}{SampleWeight(g)}$$

Where:

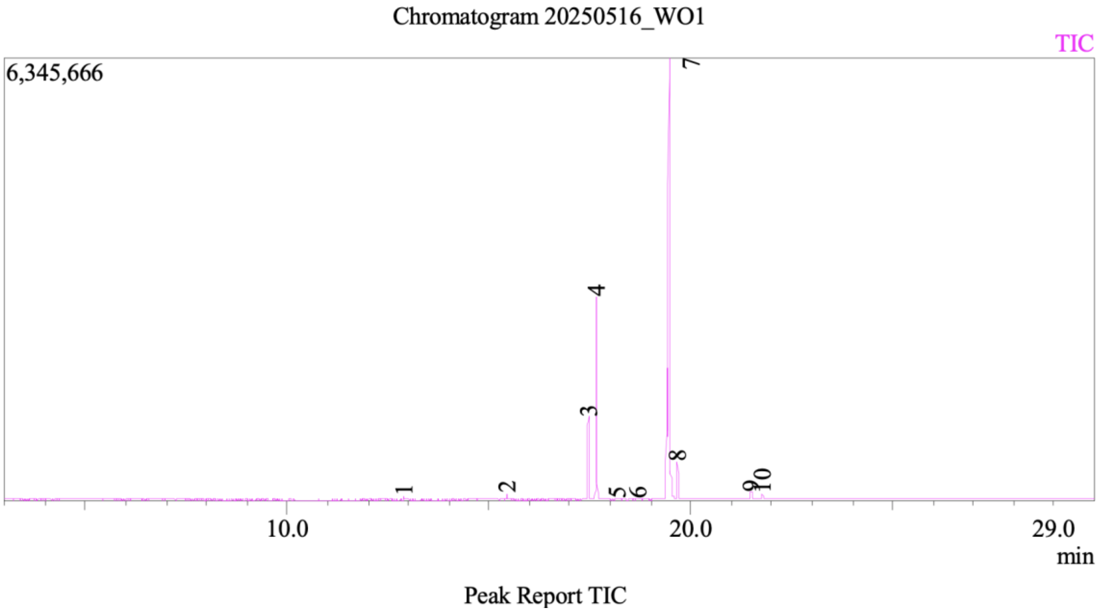
- VB = volume of HCl used in the blank (ml).
- VS = volume of HCl used in the sample (ml).
- N = normality of the HCl solution.
- 56.1 = equivalent weight of potassium hydroxide (KOH).

4. Results

In this section, the results obtained from each of the conducted tests are presented, analyzed, and discussed in detail. Each experiment has been performed with the aim of evaluating the suitability of the selected feedstocks for biodiesel production.

4.1 GCMS

The GC-MS (Gas Chromatography-Mass Spectrometry) analysis, following the derivatization process, reveals the profile of fatty acid methyl esters (FAMEs) present in each sample. This derivatization step is essential to convert the original fatty acids into their more volatile methyl ester forms, which can be detected and quantified by GC-MS[86]. Each FAME identified can then be traced back to its corresponding original fatty acid in the unprocessed oil. This analysis not only helps to characterize the chemical composition of the oils but also allows for the evaluation of their potential as biodiesel feedstocks by understanding the impact of degradation and usage on their fatty acid profiles. Total Ion Chromatograms (TICs) and corresponding tables for each of the three samples—Croton oil, degraded Croton oil, and Waste Cooking Oil (WCO)—are presented:

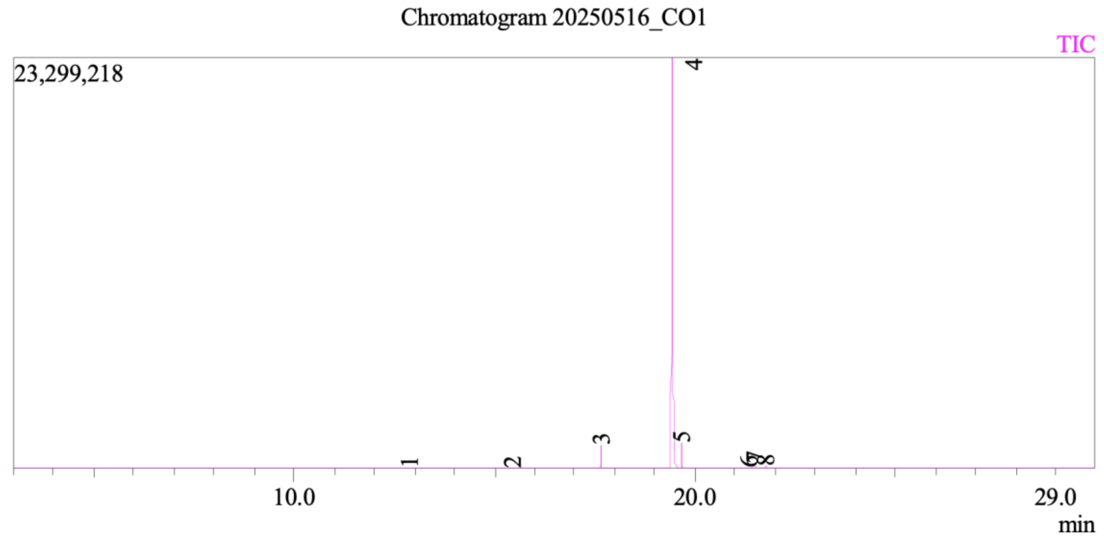

Chromatogram 20250516_WO1

Peak Report TIC

Figure 15 - TIC WCO

Peak#	**R. Time**	**Area**	**Area%**	**Name**
1	12.887	86,612	0.37	2,4-Di-tert-butylphenol
2	15.438	148,895	0.63	Methyl tetradecanoate
3	17.460	1,967,184	8.34	10-Nonadecenoic acid, methyl ester
4	17.658	4,938,122	20.93	Hexadecanoic acid, methyl ester
5	18.175	25,764	0.11	Dibutyl phthalate
6	18.687	21,395	0.09	Hexadecanoic acid, 14-methyl-, methyl ester
7	19.454	15,120,410	64.10	10-Octadecenoic acid, methyl ester
8	19.668	871,737	3.70	Methyl stearate
9	21.494	232,053	0.98	cis-11-Eicosenoic acid, methyl ester
10	21.767	176,899	0.75	Methyl 18-methylnonadecanoate

Table 1 - TIC WCO



Peak Report TIC

Figure 16 - TIC degrade croton oil

Peak#	**R. Time**	**Area**	**Area%**	**Name**
1	12.889	39,807	0.07	2,4-Di-tert-butylphenol
2	15.438	46,991	0.08	Methyl tetradecanoate
3	17.659	1,553,377	2.61	Hexadecanoic acid, methyl ester
4	19.438	54,290,993	91.15	9,12-Octadecadienoic acid, methyl ester
5	19.673	2,371,374	3.98	Methyl stearate
6	21.341	157,258	0.26	Z, Z-3,13-Octadecadien-1-ol
7	21.498	804,029	1.35	cis-Methyl 11-eicosenoate
8	21.770	295,792	0.50	Methyl 18-methylnonadecanoate

Table 2 - TIC degraded croton oil

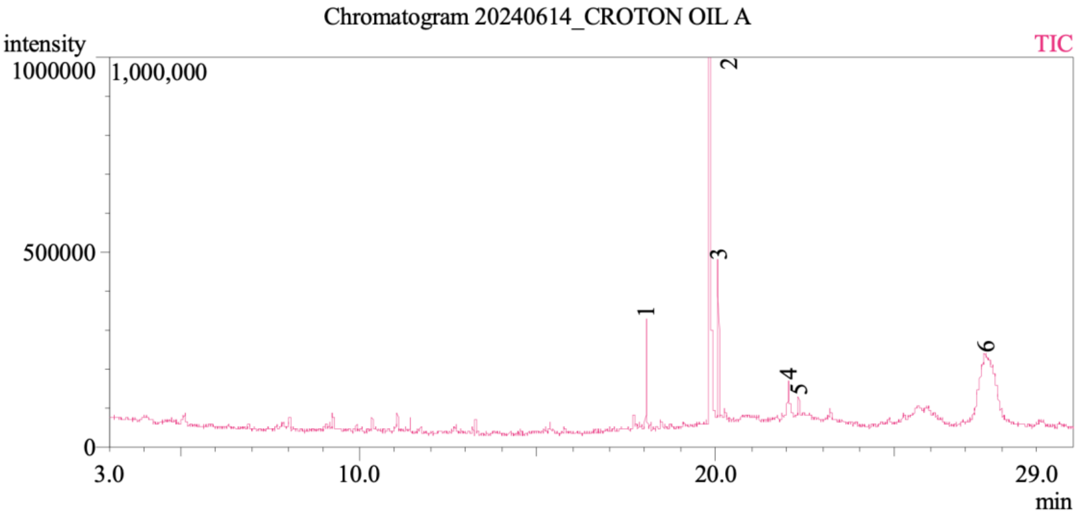


Figure 17 - TIC non degraded croton oil

The graph clearly illustrates that, compared to the degraded sample, the distribution of compounds in the fresh sample is broader. As shown in the table below, the presence of methyl linoleate is reduced to around 60%. Notably, the second most prominent component, making up approximately 30% of the sample, is 24-Norursa-3,12-dien-11-one. This suggests that, in addition to common fatty acids, the oil contains significant bioactive compounds. These unique constituents may contribute to its medicinal properties and indicate potential applications beyond biodiesel production.

Peak#	R. Time	Area	Area%	Name
1	18.046	552,232	2.94	Pentadecanoic acid, 14-methyl-, methyl ester
2	19.810	11,344,251	60.48	9,12-Octadecadienoic acid, methyl ester
3	20.066	784,029	4.18	Methyl stearate
4	22.035	334,719	1.78	cis-Methyl 11-eicosenoate
5	22.317	132,974	0.71	Methyl 18-methylnonadecanoate
6	27.555	5,608,122	29.90	24-Norursa-3,12-dien-11-one

Table 3 - TIC non degraded croton oil

Gathering all the results in a table:

Compound	*Area % (Croton Oil)*	*Area % (Degraded Croton Oil)*	*Area % (WCO)*
Pentadecanoic acid, 14-methyl-, methyl ester	*2.94*	*0.07*	*0.09*
9,12-Octadecadienoic acid, methyl ester	*60.48*	*91.15*	*0.63*
Methyl stearate	*4.18*	*3.98*	*3.70*
cis-Methyl 11-eicosenoate	*1.78*	*1.35*	*0.98*
Methyl 18-methylnonadecanoate	*0.71*	*0.50*	*0.75*
24-Norursa-3,12-dien-11-one	*29.90*	*-*	*-*
2,4-Di-tert-butylphenol	*-*	*0.07*	*0.37*
Methyl tetradecanoate (Methyl myristate)	*-*	*0.08*	*0.63*
Hexadecanoic acid, methyl ester (Methyl palmitate)	*-*	*2.61*	*20.93*
Z, Z-3,13-Octadecadien-1-ol	*-*	*0.26*	*-*
10-Nonadecenoic acid, methyl ester	*-*	*-*	*8.34*
Dibutyl phthalate	*-*	*-*	*0.11*
10-Octadecenoic acid, methyl ester	*-*	*-*	*64.10*

Table 4 - comparative analysis TIC

Results are commented considering the original fatty acids before derivatization. The most abundant component identified in non-degraded Croton oil is 9,12-Octadecadienoic acid, methyl ester (Methyl linoleate), which corresponds to linoleic acid, a polyunsaturated fatty acid. It makes up 60.48% of the total fatty acid profile, highlighting its significant contribution to the oil's composition. This high concentration suggests that Croton oil could have a good balance of unsaturation, which is favorable for biodiesel production due to better cold flow properties[86]. Other notable fatty acids include Methyl stearate (4.18%), corresponding to stearic acid, and cis-Methyl 11-eicosenoate (1.78%), corresponding to eicosenoic acid in the original oil. These fatty acids contribute to the oil's stability and overall profile, adding both saturated and unsaturated characteristics. Methyl stearate provides oxidative stability, while eicosenoate contributes to the oil's fluidity. Minor components such as Pentadecanoic acid, 14-methyl-, methyl ester (2.94%), and Methyl 18-methylnonadecanoate (0.71%) add to the complexity of the oil but do not significantly alter the primary fatty acid profile. The presence of 24-Norursa-3,12-dien-11-one (29.90%) is unusual and may suggest specific minor constituents that contribute to the oil's unique properties.

In the degraded sample, the proportion of 9,12-Octadecadienoic acid, methyl ester (Methyl linoleate) increases to 91.15%. This indicates a selective degradation of other components, leading to a higher relative concentration of linoleic acid. This change could imply that the degradation process primarily affected the minor and less stable components[86]. The concentration of Methyl stearate slightly decreases to 3.98%, while cis-Methyl 11-eicosenoate remains relatively stable at 1.35%. The reduction in these components might be due to oxidative degradation or hydrolysis, common in storage and aging processes of oils, which can affect the saturation balance and overall stability. The presence of 2,4-Di-tert-butylphenol (0.07%) and Z, Z-3,13-Octadecadien-1-ol (0.26%) in the degraded oil suggests the formation of secondary oxidation products. The overall increase in linoleic acid percentage could be due to the breakdown of other fatty acids into secondary compounds.

The most abundant component in WCO is 10-Octadecenoic acid, methyl ester (Methyl oleate), corresponding to oleic acid, which constitutes 64.10% of the fatty acid profile. This indicates a high degree of monounsaturation, which can provide good oxidative stability but might result in poor cold flow properties. Other significant components include Hexadecanoic acid, methyl ester (Methyl palmitate) at 20.93% and 10-Nonadecenoic acid, methyl ester at 8.34%. These components suggest that WCO has a complex mixture of both saturated and unsaturated fatty acids. The relatively high proportion of methyl palmitate can indicate a higher saturation level, which could enhance the oil's stability but might affect its suitability for biodiesel due to potential solidification issues at lower temperatures[86]. The presence of minor components like 2,4-Di-tert-butylphenol (0.37%) and Dibutyl phthalate (0.11%) indicates potential contamination from cooking processes and additives. These compounds do not significantly impact the overall fatty acid profile but highlight the necessity of pretreatment before converting WCO into biodiesel to remove impurities. The presence of Hexadecanoic acid, 14-methyl-, methyl ester (0.09%) and Methyl tetradecanoate (0.63%) suggests a complex origin of the oil, potentially from a blend of different cooking oils. These components, while present in small amounts, add to the diverse nature of WCO and can influence its overall properties, such as viscosity and oxidation stability.

The comparison of the fatty acid profiles of Croton oil, degraded Croton oil, and WCO reveals significant changes in the composition due to degradation and usage. Croton oil shows a high concentration of polyunsaturated fatty acids, making it suitable for biodiesel production with good cold flow properties. Degraded Croton oil shows increased dominance of linoleic acid, indicating selective degradation. In contrast, WCO is rich in oleic acid, providing better stability but requiring careful pretreatment due to potential contaminants. These insights help assess the suitability of these oils as feedstocks for biodiesel production.

4.2 FTIR

FTIR analysis provides a comprehensive understanding of the chemical composition of Croton megalocarpus oil and waste cooking oil (WCO) by identifying key functional groups essential for biodiesel production. This method also allows for the detection of oxidation products and assessment of oil purity, which are crucial factors in evaluating the quality and suitability of these oils as biodiesel feedstocks. In the following section, the spectra are presented and analyzed, highlighting the relevant functional groups and their implications for biodiesel production.

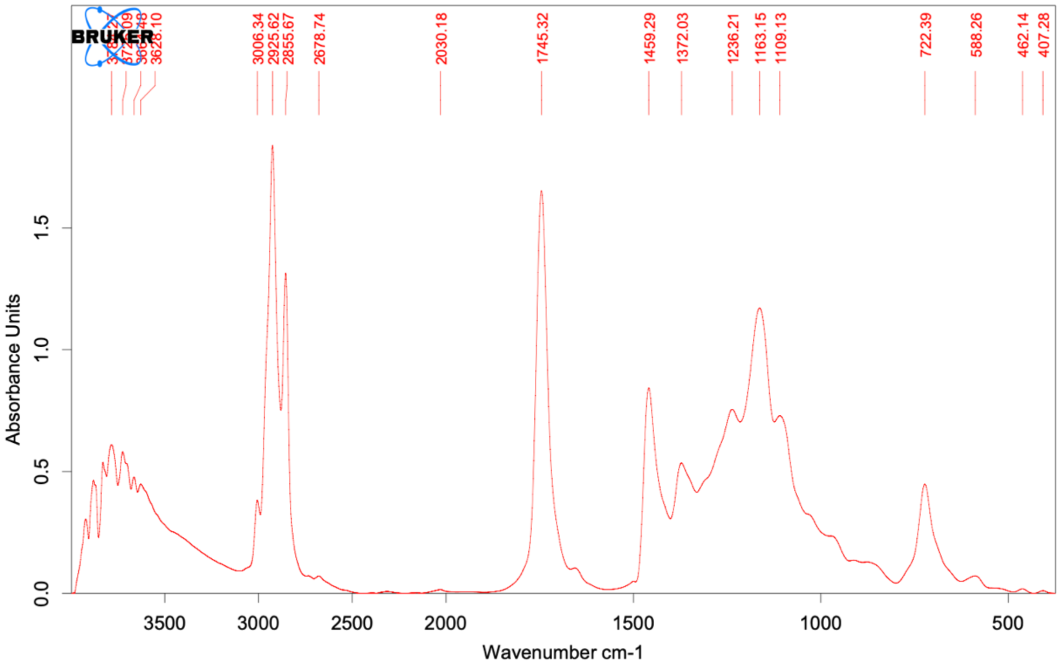


Figure 18 - FTIR spectrum WCO

Waste Cooking Oil (WCO)

The FTIR spectrum of WCO shows the following key functional groups:

- C-H Stretching (2850-2950 cm^{-1}): The breadth and intensity of the peaks in this region confirm the presence of long saturated and unsaturated hydrocarbon chains, typical of fatty acids and triglycerides found in cooking oil.
- C=O Stretching (1735-1750 cm^{-1}): The presence of a strong and sharp peak in this region indicates a high concentration of ester functional groups, confirming the presence of triglycerides and oxidation products such as aldehydes and ketones.
- C-H Bending (1460-1470 cm^{-1}, 1370-1380 cm^{-1}): These peaks correspond to the bending vibrations of CH_2 and CH_3 groups in aliphatic chains, which are characteristic of fatty acids.
- C-O Stretching (1050-1250 cm^{-1}): The presence of peaks in this region indicates the presence of ester bonds, typical in triglycerides and transesterification products, consistent with the origin of waste cooking oil.

- Out-of-Plane Bending (~720 cm^{-1}): This peak is associated with the C-H bonds in long-chain hydrocarbons, confirming the presence of long aliphatic chains.

The intensity and clarity of these peaks suggest that the waste cooking oil still contains a significant number of triglycerides despite previous usage[89].

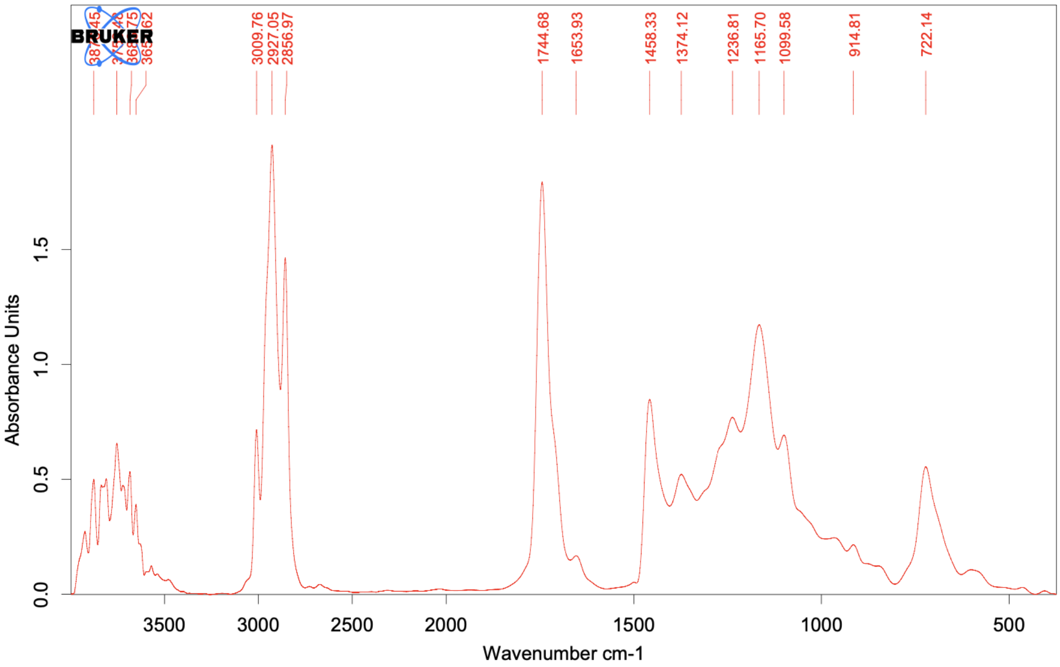


Figure 19 - FTIR spectrum non degraded croton oil

Croton Oil (Non-Degraded)

The FTIR spectrum of non-degraded Croton oil shows:

- C-H Stretching (2850-2950 cm^{-1}): Similar peaks to those observed in WCO, indicating the presence of long saturated and unsaturated hydrocarbon chains typical of fatty acids present in Croton oil.
- C=O Stretching (1735-1750 cm^{-1}): A very pronounced peak, suggesting a high concentration of triglycerides, indicating that the oil is in a non-oxidized and non-degraded state.
- C-H Bending (1460-1470 cm^{-1}, 1370-1380 cm^{-1}): Well-defined peaks that confirm the presence of methyl and methylene groups, characteristic of aliphatic chains.

- C-O Stretching (1050-1250 cm^{-1}): The clear peaks confirm the ester structure of the triglycerides present in Croton oil.
- Out-of-Plane Bending (~720 cm^{-1}): This peak indicates the presence of long aliphatic chains, common in unsaturated compounds like linoleic acid.

The spectrum suggests a relatively stable oil, with a predominance of intact triglycerides.

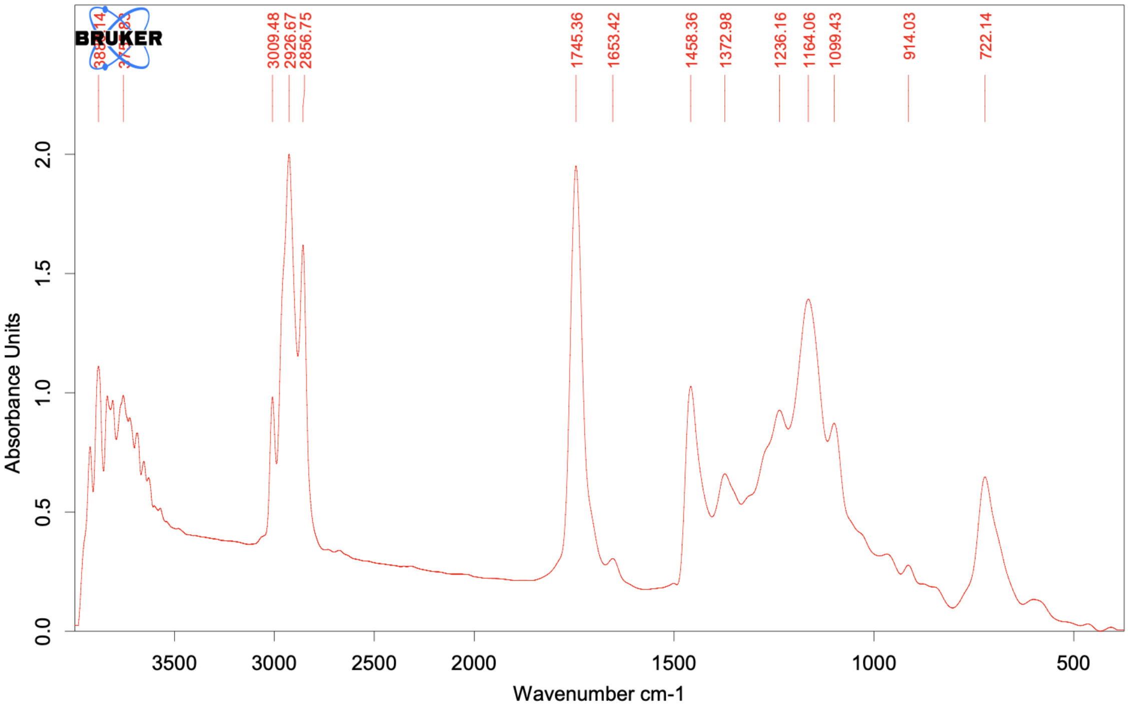


Figure 20 - FTIR spectrum degraded croton oil

Croton Oil (Degraded)

The FTIR spectrum of degraded Croton oil shows:

- C-H Stretching (2850-2950 cm^{-1}): The peaks are less defined compared to the non-degraded oil, suggesting possible alterations in the hydrocarbon chains.
- C=O Stretching (1735-1750 cm^{-1}): A more intense peak compared to the non-degraded oil, indicating a higher presence of oxidation products, such as aldehydes and ketones, formed during oxidative degradation.
- C-H Bending (1460-1470 cm^{-1}, 1370-1380 cm^{-1}): The intensity of these peaks is reduced, suggesting a possible breakdown of aliphatic chains.

- C-O Stretching (1050-1250 cm^{-1}): The peaks are present but with altered intensity, indicating a partial breakdown of ester bonds.
- Out-of-Plane Bending (~720 cm^{-1}): While still present, the peak is reduced, indicating that some of the long aliphatic chains are still present but in lower quantities compared to the non-degraded oil.

The comparison between the two Croton oil samples highlights clear signs of oxidation, as evidenced by the increased intensity of the C=O peak and the reduced C-H bands, indicating the degradation of triglycerides.

The degraded sample shows a more pronounced C=O stretching peak (1735-1750 cm^{-1}), pointing to a higher presence of oxidation products, while the diminished C-H stretching and bending peaks suggest the breakdown of aliphatic chains due to oxidative activity. The reduced intensity of the C-O stretching in the degraded oil further indicates partial disruption of ester bonds.

Moreover, the increased absorbance around 3400 cm^{-1} confirms the formation of hydroxyl-containing compounds, a typical sign of oxidative degradation[89]. Despite this, the core triglyceride structure of Croton oil remains largely intact, with fewer oxidation by-products compared to Waste Cooking Oil (WCO).

When comparing Croton oil to WCO, significant differences in their chemical profiles emerge. The WCO spectrum reveals a more complex composition, with prominent peaks in the C-H stretching region and heightened intensity in the C-O stretching region, indicative of various compounds formed through repeated heating and cooking processes. This complexity suggests a chemically heterogeneous mixture with a diverse range of fatty acids and potential contaminants or degradation products[89]. In contrast, both the non-degraded and degraded Croton oil samples exhibit a simpler and more stable composition. The non-degraded Croton oil displays distinct peaks in the C-H and C-O stretching regions, signifying a higher proportion of intact triglycerides and fewer degradation indicators, making it more suitable for biodiesel production.

Even though the degraded Croton oil shows increased C=O intensity like WCO, it maintains a more uniform chemical profile. This uniformity suggests that, despite degradation, Croton oil retains a consistent fatty acid composition, which is beneficial for biodiesel production.

Overall, while both oils have potential as biodiesel feedstocks, Croton oil, particularly in its non-degraded state, offers a simpler and more consistent chemical profile. This makes it more predictable and potentially more efficient for conversion into biodiesel compared to the chemically diverse and more degraded WCO.

4.3 Density

The density measurements for Croton oil, waste cooking oil (WCO), and diesel are presented in the table below:

sample	Density [kg/m3]
Croton oil	896,583
WCO	902,833
Diesel	838,733

Table 5 - density measurements

The higher densities of Croton oil and WCO compared to diesel suggest potential differences in fuel injection and combustion characteristics. Their similar densities indicate they may behave similarly during biodiesel production, impacting yield and fuel properties[91].

4.4 Kinematic Viscosity

Following the described procedure, the kinematic viscosity values of Croton oil, waste cooking oil (WCO), and diesel were determined at both room temperature and 40°C. These results are summarized in the table below for comparison.

Oil Sample	Viscosity at Room Temperature (cSt)	Viscosity at 40°C (cSt)
Croton Oil	43.41	23.82
WCO	70.48	33.60
Diesel	2.18	0.97

Table 6 - kinematic viscosity measurements

The kinematic viscosity results show a clear dependency on temperature across all samples, with a noticeable decrease as temperature increases. Croton oil's viscosity drops from 43.4 cSt at room temperature to 23.8 cSt at 40°C, which is within the typical range for vegetable oils used as biodiesel feedstocks. According to the literature, vegetable oils generally have viscosities between 30-50 cSt at room temperature, and their reduction with temperature makes them more manageable for fuel processing[92]. WCO, with viscosities of 70 cSt at room temperature and 33.6 cSt at 40°C, displays a higher initial viscosity due to degradation and impurities from repeated use. This high viscosity can cause complications in fuel injection systems and engine performance without appropriate modification or processing. Diesel, with viscosities of 2.17 cSt at room temperature and 0.9 cSt at 40°C, falls within the standard range for diesel fuels, which is typically between 1.5-4.0 cSt at 40°C according to ASTM D975 standards. The lower viscosity of diesel compared to vegetable oils contributes to its superior flow characteristics and ease of use in engines without modification.

The pronounced viscosity decreases with increasing temperature for both Croton oil and WCO underscores the need for appropriate temperature management or chemical modification, such as transesterification, to achieve fuel properties compatible with standard diesel engines.

4.5 Higher Heating Value

These measurements give an indication of how much energy can be extracted from the samples during combustion, which is vital for evaluating their use as alternative fuels.

Sample	HHV (q[J/g])
Croton Oil	41180.1631
WCO	41530.3487
Diesel	44031.1302

Table 7 - HHV measurements

The higher heating values (HHV) of Croton oil, waste cooking oil (WCO), and diesel reveal some notable differences. Croton oil has an HHV of 41,180 J/g, which is consistent with the typical range for vegetable oils, generally between 39,000 and 42,000 J/g. This indicates that Croton oil has good energy potential as a biodiesel feedstock, although slightly lower than diesel. WCO, with an HHV of 41,530 J/g, shows a slightly higher value than Croton oil, potentially due to additional hydrocarbons or impurities from the cooking process. This value still falls within the expected range for used vegetable oils, confirming its suitability for biodiesel production[102]. Diesel, on the other hand, has an HHV of 44,031 J/g, which aligns with its typical range of around 44,000 to 46,000 J/g. This higher HHV indicates a greater energy content per unit mass compared to vegetable oils, leading to better efficiency in combustion engines. The lower HHV of vegetable oils compared to diesel suggests that while they are viable as biodiesel feedstocks, their lower energy density must be considered when blending or modifying them to achieve performance closer to that of conventional diesel.

4.6 Acid Value

The titration results revealed significant differences in the acid values of the analyzed samples, which are crucial for determining their suitability as biodiesel feedstocks.

Sample	Acid Value (mg KOH/g)
Degraded Croton Oil	19,17
New Croton Oil	4,48
WCO	3,57

Table 8 - AV measurements

The degraded Croton oil sample had an acid value of 19.17 mg KOH/g, far exceeding the typical range for fresh vegetable oils, which is generally between 0.5 and 6 mg KOH/g. This high value, likely due to oxidation and hydrolysis, indicates a substantial presence of free fatty acids (FFAs), complicating its use for biodiesel production without pretreatment[50]. In contrast, the new Croton oil sample showed a much lower acid value of 4.48 mg KOH/g, indicating good quality and minimal degradation, making it more suitable for direct conversion into biodiesel.

The waste cooking oil (WCO) sample had an acid value of 3.57 mg KOH/g, which, while still above the recommended maximum of 0.5 mg KOH/g set by ASTM D6751 and EN 14214 standards, is relatively common for used oils and manageable with appropriate pretreatment.

These standards are critical because exceeding the maximum acid value can lead to soap formation during transesterification, reducing the yield and quality of the biodiesel[72]. Therefore, both the degraded Croton oil and WCO require pretreatment, such as esterification, to lower their acid values before biodiesel production to meet the required specifications and optimize the process efficiency.

4.7 Moisture Content

The following table presents the measured moisture content for Croton megalocarpus oil and waste cooking oil (WCO):

Oil Sample	Moisture Content (%)
Croton megalocarpus oil	0.07
Waste Cooking Oil (WCO)	0.24

Table 9 - moisture content measurements

The moisture content of Croton oil was found to be 0.07%, lower than the typical 0.17% value, which is advantageous for minimizing issues like soap formation during transesterification[97]. In contrast, WCO showed a moisture content of 0.24%, which, although typical for used oils, exceeds the maximum limit of 0.05% set by ASTM D6751 and EN 14214 standards. Reducing the moisture content in WCO is crucial to prevent hydrolysis and ensure efficient biodiesel production.

4.8 Iodine value

The experimental iodine numbers for Croton megalocarpus oil and waste cooking oil (WCO) are presented in the table below.

Oil Sample	Iodine Value (g I_2/100 g)
Croton megalocarpus oil	150.58
Waste Cooking Oil (WCO)	136.33

Table 10 - Iodine number measurements

The iodine value of 150.58 g I_2/100 g for Croton oil indicates a high degree of unsaturation, which is above the typical value of around 139 g I_2/100 g reported in literature. This high level of unsaturation can improve cold flow properties but also increases the risk of oxidative instability[99]. Similarly, the iodine value for WCO is 136.33 g I_2/100 g, higher than the usual range of 83-101 g I_2/100 g, reflecting its diverse fatty acid composition from repeated use. Both values exceed the EN 14214 standard recommendation of less than 120 g I_2/100 g for biodiesel feedstocks, indicating potential challenges with oxidative stability that may affect long-term fuel quality.

4.9 Pour Point

The following table presents the measured pour points for each oil sample, determined using the AOCS Cc 11-53 standard

Oil Sample	Measured Pour Point (°C)
Waste Cooking Oil (WCO)	3.7 - 4.9
Croton Oil	0.8 - 0.9

Table 11 - pour point measurements

The measured pour points for the analyzed oil samples highlight their suitability for biodiesel production in various temperature conditions. The waste cooking oil (WCO) showed pour point values ranging from 3.7°C to 4.9°C.

These values align with typical ranges for used cooking oils, which can vary widely but are generally reported between 0°C and 15°C, depending on the degree of saturation and thermal degradation from repeated use. Such pour points suggest that WCO may face challenges in colder climates without additional processing or blending with lower pour point biodiesel.

For Croton oil, the pour point values obtained were between 0.8°C and 0.9°C, which are lower than the average values typically found in literature for this oil, which range from 3°C to 4°C.

This lower-than-expected pour point indicates that the specific Croton oil samples tested have better cold flow properties than usual. This could be due to a lower content of saturated fatty acids or differences in oil composition, enhancing its performance in cooler conditions[103].

Overall, while both oils show potential for biodiesel production, their pour points suggest that they may require modifications, such as the addition of cold flow improvers, to meet performance standards in colder climates and to ensure that they remain fluid and functional at low temperatures.

4.10 Peroxide Value

Peroxide value measures the peroxide compounds formed due to oxidation, with higher values indicating more oxidation and, consequently, a reduced quality of the oil or fat. Results are summarized in the following table:

Oil Sample	Peroxide Value (mEq/kg)
Fresh Croton Oil	9.01 - 11.54
Degraded Croton Oil	1.93 - 2.78
Waste Cooking Oil	15.06 - 17.21

Table 12 - peroxide value measurements

Fresh Croton oil exhibits a peroxide value of 2 mEq/kg, which is well below the typical maximum of 10 mEq/kg for fresh vegetable oils, indicating minimal oxidation and good storage quality.

WCO sample, with a peroxide value of 10 mEq/kg, falls within the lower end of the expected range for used oils, which can typically vary from 10 to 30 mEq/kg depending on usage and storage conditions. This suggests moderate oxidation, still manageable for biodiesel production, but potentially requiring pretreatment to remove oxidation products.

During the initial titration of the Croton oil sample, a very high acid value was detected, indicating significant degradation. To confirm this result, a fresh sample of Croton oil was obtained and reanalyzed, revealing a much lower acid value. This difference is likely related to the subsequent peroxide value findings, where the degraded Croton oil exhibited considerably higher peroxide values (15-17 mEq/kg) compared to the fresh sample.

The elevated peroxide and acid values in the degraded oil suggest advanced primary oxidation and substantial degradation, aligning with the initial observations made during titration. Such elevated peroxide levels indicate the presence of peroxides and hydroperoxides, which can negatively impact biodiesel stability and quality, making it necessary to reduce these levels before production[95].

4.11 Saponification Value

The results of the saponification value test for the oil samples, indicating the amount of KOH required to saponify one gram of each sample, are summarized in the following table.

Oil Sample	Measured Saponification Value (mg KOH/g)	Typical Saponification Value (mg KOH/g)
Croton Oil	104 - 112	190 - 200
Waste Cooking Oil	138 - 165	180 – 195

Table 13 - comparation between measured and typical saponification values

The measured saponification values for Croton oil range from 104 to 112 mg KOH/g, which is significantly lower than the typical range of 190 to 200 mg KOH/g found in the literature.

A lower saponification value indicates the presence of triglycerides with higher molecular weights, meaning they have longer fatty acid chains. This can impact the biodiesel production process as these larger molecules are more challenging to break down during transesterification[104]. Additionally, lower values may suggest the presence of fewer saponifiable triglycerides, potentially indicating that the oil contains a higher proportion of non-triglyceride components, such as free fatty acids or degradation products, which can complicate the reaction and reduce biodiesel yield[68].

For waste cooking oil (WCO), the measured values range from 138 to 165 mg KOH/g, which are also lower than the typical range of 180 to 195 mg KOH/g. This suggests that the WCO sample may have undergone thermal degradation, resulting in the formation of longer-chain triglycerides or non-saponifiable materials. The saponification value is crucial for determining the catalyst requirement during transesterification.

Oils with lower saponification values may require more stringent control over reaction conditions to ensure efficient conversion to biodiesel. In both cases, the lower-than-expected saponification values highlight the need for careful optimization of the transesterification process to achieve complete conversion and maximize biodiesel yield. This parameter is essential for understanding the composition and reactivity of the oils, ultimately influencing the efficiency and quality of biodiesel production.

4.12 Suitability for biodiesel production

The suitability of *Croton megalocarpus* oil and waste cooking oil (WCO) for biodiesel production was evaluated based on their physicochemical properties and the outcomes of base-catalyzed transesterification experiments. The characterization aimed to identify how these properties influenced the transesterification process and to address the significant challenges encountered during the experimental phase. The limitations of the equipment used further complicated the process, highlighting the need for a more controlled environment to achieve reliable results.

The transesterification process faced considerable difficulties due to equipment limitations that affected crucial reaction parameters. Maintaining a stable reaction temperature was challenging, with fluctuations of ±10°C, which made it difficult to control the reaction kinetics and achieve optimal conversion. Precise temperature control is essential in transesterification because even minor deviations can influence the reaction rate and the formation of undesirable by-products like soaps[68]. The inconsistency in stirring speed also affected the uniformity of the reaction environment, leading to problems with phase separation between the biodiesel and glycerin layers[69]. Accurate measurement of catalyst concentrations posed additional challenges, resulting in significant variability in catalyst-to-oil ratios across different trials. These issues collectively made it impractical to implement a more suitable two-step acid-base transesterification process, which typically involves an initial acid-catalyzed esterification to reduce free fatty acids (FFAs) followed by base-catalyzed transesterification[74].

The direct approach, which was adopted out of necessity, is less efficient for oils with high FFA levels, as FFAs react with the base catalyst to form soaps. Soap formation was a recurrent issue, disrupting the separation of biodiesel from the glycerin phase and even causing phase inversion in some cases, where the expected biodiesel phase appeared denser than the glycerin phase. Such occurrences indicate that without pre-treatment to reduce the acid value, high-FFA oils are unsuitable for direct base-catalyzed transesterification.

Characterizing the properties of *Croton* oil and WCO provided insight into the reasons behind the transesterification difficulties.

- **Acid Value and FFA Content**: Both oils exhibited high acid values, particularly in degraded *Croton* oil samples, where prolonged storage under poor conditions had led to oxidative degradation. High FFA content complicates the transesterification process because it reacts with the basic catalyst to produce soaps, thereby consuming the catalyst and reducing its effectiveness. The presence of FFAs also contributes to emulsification during the separation stage, further complicating the isolation of the biodiesel phase[104]. Research suggests that pre-treatment techniques like acid esterification are crucial for lowering the acid value and improving the process efficiency for high-FFA oils.

- **Fatty Acid Composition and Oxidative Stability**: The GC-MS analysis showed that *Croton* oil contains a balanced mix of saturated and unsaturated fatty acids, which provided moderate oxidative stability. In contrast, WCO had a higher degree of unsaturation due to repeated heating during cooking, making it more prone to oxidation[50]. The elevated peroxide values measured in both oils further indicated the presence of oxidation by-products, which can lead to increased viscosity and the formation of deposits[95]. Using antioxidants during biodiesel production could mitigate these effects by stabilizing the fuel and preventing further oxidative degradation. Studies have highlighted the role of natural antioxidants like tocopherols in improving the oxidative stability of biodiesel derived from unsaturated oils[73].
- **Moisture Content and Impurities**: Both oils showed significant moisture content, with WCO displaying higher levels due to its origin as a used cooking oil. Moisture can hydrolyze triglycerides during the reaction, leading to soap formation and increasing the FFA content[97]. This issue underscored the importance of drying the oils prior to transesterification to minimize water content and reduce its impact on the reaction. Techniques such as silica gel drying and the use of molecular sieves are recommended for achieving moisture levels below 0.05%, which aligns with international biodiesel standards[105].
- **Cold Flow Properties and Viscosity**: The level of saturation in fatty acids affects the cold flow characteristics of biodiesel. *Croton* oil's fatty acid profile, with its moderate saturation, offered better cold flow properties than more saturated oils, although it required additional treatments like cold flow improvers for use in colder environments[65]. The transesterification process effectively reduced the viscosity of the oils to levels compatible with diesel engine requirements. Ensuring consistent control over reaction conditions would have further optimized viscosity and cold flow properties, enabling better performance of the biodiesel in real-world applications[92].

Chemical-physical properties	**Definition**	**Effects**
Density	Amount of mass per unit of volume	Injectors' performance can be affected
Viscosity	Resistance of a fluid to flow	Impact on fuel feeding and injection. Severe effect on fuel atomization
Calorific Value	Energy from fuel combustion	Directly related to energy performances
Cetane number	Ignition behaviour	Impact on engine performances and control, cold start, noise, emissions
Flash point	Min T at which the fuel vapors ignite in presence of an ignition mean (flame)	Impact on storage safety
Peroxide value	Related to heavy deposit formation under certain condition of T and p, in presence of oxygen	Risk of viscosity increase
Water content	It measures the water content	Impact on fuel filters and metallic part (corrosion) lifetime
Acid Value	It indicates the presence of Free Fatty Acids	At high T acids generate salts with metallic parts, and can damage the engine or the tanks
Iodine value	It is related to the unsaturation degree of the oil	Impact on fuel behaviour and stability
Saponification nr	Content of FFA or FA linked to the glycerol of a VO	Impact on fuel behaviour and stability

Table 14 - influence of measured properties on fuel's quality

The study did not measure critical fuel properties such as the Cetane Number (CN) and flash point due to equipment limitations. The CN, which indicates a fuel's ignition delay, is a key factor in determining engine performance and cold start capabilities. Standard diesel typically has a CN of 48 or higher, while biodiesel produced from oils like *Croton* can have values ranging between 50 and 55, depending on the fatty acid composition. Measuring the CN would have provided insights into the combustion quality of the produced biodiesel. Similarly, the flash point, which determines the temperature at which the fuel can ignite, is vital for safe storage and handling[102]. Biodiesel generally has a flash point between 110°C and 160°C, significantly higher than conventional diesel, thus posing fewer safety risks. The inability to assess these properties limits the understanding of the produced biodiesel's overall quality. The challenges encountered in this study highlight the complexity of biodiesel production from high-FFA feedstocks like *Croton megalocarpus* oil and WCO, especially under equipment-limited conditions. Issues such as high acid values, moisture content, soap formation, and phase separation were prevalent, making the direct base-catalyzed transesterification process inefficient without pre-treatment. The findings emphasize the need for more advanced equipment to control reaction parameters accurately, such as temperature and stirring speed, as well as pre-treatment methods to reduce FFAs. Addressing these aspects will be crucial for improving biodiesel yields and meeting quality standards. Future work should focus on refining the transesterification process through two-step methods.

Conclusions

This thesis has examined the suitability of *Croton megalocarpus* oil and waste cooking oil (WCO) as feedstocks for biodiesel production in Kenya. The study aimed to assess the feasibility of these oils by evaluating their chemical properties, the challenges encountered during the transesterification process, and the broader environmental and socioeconomic implications. While the results demonstrated that both feedstocks are viable candidates for biodiesel, significant challenges arose, primarily due to high free fatty acid (FFA) content and equipment limitations that affected process consistency and biodiesel quality.

The research encountered substantial difficulties due to the high acidity of the oils, especially in degraded *Croton* samples, where extended storage had led to oxidative degradation. The elevated acid value indicated the presence of significant FFA levels, which disrupted the base-catalyzed transesterification process by causing soap formation and leading to phase separation issues. These problems were further exacerbated by equipment constraints, such as inconsistent temperature control (fluctuations of ±10°C) and difficulties in accurately measuring catalyst concentrations. As a result, the planned optimization of reaction parameters—including reaction time, temperature, methanol-to-oil ratio, and catalyst dosage—could not be effectively achieved, compromising the yield and reproducibility of the biodiesel production.

Given these challenges, the implementation of a two-step acid-base transesterification approach would be more suitable for high-FFA oils, as it allows for initial FFA reduction through acid esterification followed by base-catalyzed transesterification[68]. However, this method was not feasible under the given experimental conditions, which led to the adoption of direct transesterification. While increasing the methanol-to-oil ratio helped neutralize some FFAs, the process remained inefficient due to the high soap formation rates and resulting phase inversion during several trials. Research on non-edible oils has shown that pre-treatment of high-FFA feedstocks is essential for improving transesterification efficiency and biodiesel yield, as indicated by similar studies [104], [106] .

In this study, several properties of *Croton* oil and WCO significantly influenced the transesterification process. These properties included acid value, peroxide value, fatty acid composition, viscosity, and moisture content, which have direct implications on biodiesel quality:

The elevated acid values measured in the oils, especially in degraded *Croton*, revealed the need for pre-treatment to avoid soap formation during transesterification. High FFA levels result in catalyst deactivation, which further impairs the reaction efficiency. Pre-treatment methods, such as esterification or physical adsorption, could significantly reduce acid levels, as demonstrated in biodiesel production studies involving high-FFA feedstocks[72], [96].

The analysis indicated higher peroxide values in the *Croton* oil samples due to prolonged storage under suboptimal conditions, reflecting oxidative degradation. Oxidation can lead to an increase in viscosity and the formation of insoluble materials that affect the transesterification process, and the quality of the biodiesel produced. Additives can improve the oxidative stability of biodiesel [103], [107], making them especially useful when dealing with oils that have higher unsaturation levels, like WCO.

The fatty acid profiles of the oils play a crucial role in determining biodiesel properties. *Croton* oil's balance of saturated and unsaturated fatty acids provides a compromise between cold flow properties and oxidation stability, while WCO's higher unsaturation increases its vulnerability to oxidation. Managing these characteristics is essential to meet standard biodiesel requirements, including viscosity, which influences fuel atomization and combustion efficiency[108].

Both *Croton* oil and WCO contained moisture levels that exceeded biodiesel standards, leading to hydrolysis and further FFA formation during the transesterification process[95]. Adequate drying and storage protocols are therefore critical to reducing water content and enhancing the reaction efficiency. Techniques like molecular sieves and silica gel drying can help achieve moisture levels below the accepted 0.05% threshold for biodiesel production.

Water-Energy-Food (WEF) nexus also plays a critical role in evaluating biofuel sustainability in Kenya[109]. Large-scale *Croton* cultivation could potentially strain water resources, especially in arid regions. While *Croton* is known for its drought resistance, the water requirements for biodiesel production, including irrigation and processing, must be considered to avoid exacerbating local water scarcity. Effective water management practices, such as rainwater harvesting and efficient irrigation, are essential to balance biofuel production with the needs of other sectors[110].

However, *Croton* trees' ability to sequester carbon and grow on marginal lands makes them a promising feedstock for sustainable biofuel production, especially when cultivated in regions unsuitable for food crops. Their drought resistance and capacity to improve soil quality further enhance their value as a sustainable energy crop[58]. Conversely, WCO exhibited a lower environmental footprint since it is a recycled feedstock. Its use in biodiesel production exemplifies a circular economy model, transforming waste into valuable energy and reducing the environmental impacts of fossil fuel consumption[67]. Nonetheless, the variability in WCO quality due to different cooking practices presents a challenge for standardizing biodiesel production and necessitates careful pretreatment to ensure consistent fuel properties[66].

To overcome the limitations and realize the full potential of biodiesel production from *Croton* oil and WCO, the following measures are recommended:

Adopt Advanced Catalytic Methods: Exploring the use of heterogeneous or enzymatic catalysts could improve the efficiency of the transesterification process, especially for high-FFA oils. Such catalysts can tolerate higher acidity levels and minimize soap formation[71], [106].

Implement Pre-treatment Protocols: Acid esterification or physical adsorbents should be used to lower FFA levels before base-catalyzed transesterification, thus reducing catalyst consumption and improving biodiesel yield[72], [83].

Invest in Infrastructure and Equipment: Adequate temperature control, consistent stirring mechanisms, and accurate catalyst dosing equipment are necessary to optimize reaction conditions and ensure the reproducibility of results.

Expand Regulatory Support: Strengthening Kenya’s regulatory framework by establishing biodiesel quality standards, providing incentives for biofuel production, and supporting infrastructure development can stimulate investment in the sector and ensure long-term sustainability[39].

This research highlights the significant challenges in biodiesel production from high-FFA feedstocks like *Croton* oil and WCO, as well as the need for a more controlled experimental setup to achieve higher yields and better-quality biodiesel. However, with appropriate pre-treatment techniques and advanced catalytic processes, these feedstocks offer a sustainable and locally available alternative to fossil fuels in Kenya. By aligning biodiesel production with the country's Vision 2030 objectives, Kenya can reduce its reliance on imported energy, promote rural development, and contribute to global climate goals. The path forward involves addressing technical challenges, improving policy frameworks, and fostering collaboration across sectors to unlock the full potential of biodiesel as a cornerstone of Kenya’s renewable energy strategy.

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