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Instituto **Tecnológico**
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DOCTORADO EN CIENCIAS DE LA INGENIERÍA

**"VALORIZACIÓN DE RESIDUOS DE
FILTROS DE CIGARRO COMO PRECURSORES
DE CATALIZADORES PARA LA PRODUCCIÓN
DE BIOENERGÉTICOS"**

**“Valorization of cigarette filter waste as precursors of
catalysts for biofuels production”**

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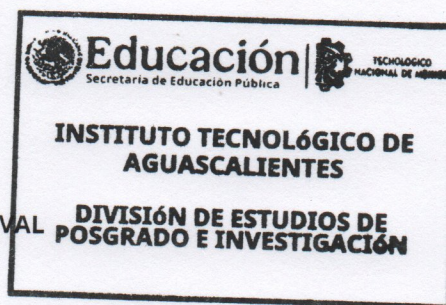
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Abstract

This thesis addresses the valorization of cigarette filter waste as a raw material for the synthesis of magnetic catalysts applied to the production of biodiesel and biolubricants, thus contributing to the energy transition and sustainable waste management. The initial chapters (1 and 2) present the current energy context, the importance of biofuels and biolubricants as renewable alternatives, as well as their properties, applications, and production techniques. In addition, the environmental impact of cigarette filter waste, considered one of the most abundant and polluting waste products worldwide, is highlighted, along with its potential use in the production of heterogeneous catalysts.

In the experimental phase (Chapters 3, 4, and 5), different synthesis routes for heterogeneous catalysts were evaluated using acetate cellulose from cigarette filters combined with magnetite particles. Processes, pyrolysis, and direct use of fibers were compared, demonstrating that the catalysts obtained through the second route presented greater catalytic efficiency, achieving conversions of up to 99.5% in the transesterification of soybean oil with methanol. Subsequently, EDTA-functionalized materials were developed through hydrothermal carbonization, which improved stability and catalytic activity, maintaining yields above 90% even after 90 days of storage, with effective reuse through four reaction cycles. Finally, the modification of the catalysts with calcium hydroxide to produce fatty acid esters of trimethylolpropane (FATE), compounds used as biodegradable lubricants, was explored, achieving conversions of up to 91.83% and with the ability to be reused in five cycles with a gradual decrease in performance.

The results confirmed that catalysts prepared from cigarette filter waste not only possess high catalytic potential but also represent a sustainable alternative that integrates waste valorization with the production of renewable energy and lubricant compounds. This research contributes to both advancements in the field of heterogeneous catalysis and the development of circular economy strategies with a positive environmental impact.

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Chapter 1. Introduction

1.1. Background

Due to population growth, the increasing demand for food, the widespread use of technological devices, and the consequent industrial development, global energy consumption has significantly increased in recent years (Dai et al., 2025). Despite major advancements in the energy sector, the energy that still supplies most countries today, covering up to four-fifths of global consumption, is based on fossil fuels such as oil, natural gas, and coal (Belay et al., 2025).

Gasoline and diesel, used mainly in the transportation sector, are derived from oil, along with other products such as lubricants, which are generally employed in machinery and the automotive industry (Brockway et al., 2019). However, the intensive and excessive use of these resources has led to serious environmental issues, including global warming caused by greenhouse gas emissions, as well as water and air pollution (Martins et al., 2019; Adebayo et al., 2021). Furthermore, fossil fuels are resources that cannot regenerate quickly; they take millions of years to form through natural processes. Therefore, their exclusive and prolonged use could lead to supply shortages and, eventually, a global energy crisis (Chien, 2022).

Considering this situation, the search for sustainable energy sources has intensified, aiming to mitigate the environmental impacts associated with fossil fuel use and reduce dependence on these energy sources (Narayanamoorthy et al., 2021). Particularly in the transportation sector, one of the most promising alternatives is biofuels, which have gained importance due to their production from renewable resources and their lower carbon footprint (Kumar et al., 2019). Among these bioenergies, biodiesel has emerged as a viable option to replace diesel fuel, thanks to its ability to blend with or completely substitute conventional fuel without requiring engine modifications (Padder et al., 2024).

In addition to the transportation sector, another area closely linked to oil is that of industrial and automotive lubricants, as most of these products are made from mineral oils derived from crude petroleum (Prasannakumar et al., 2025). Their use also poses environmental risks due to their low biodegradability and high toxicity, increasing their negative environmental impact during and after use (Nguyen et al., 2024). In this context, biolubricants emerge as a viable and less polluting alternative. Thus, the transition to renewable sources such as biofuels and biolubricants represents a fundamental strategy to mitigate the problems caused by the excessive use of conventional resources, making this one of the most relevant areas of current research (Narayanamoorthy et al., 2021).

Biodiesel and biolubricants are obtained from a fatty acid source with the aim of transforming these molecules into suitable compounds, since the direct use of vegetable oils over prolonged periods

has led to engine malfunction due to their high viscosity and low oxidative stability (Wahyudi et al., 2018).

Biodiesel, defined as a mixture of fatty acid methyl esters (FAME), is one of the most important biofuels due to its many advantages, such as biodegradability, properties like diesel, lower emission of atmospheric pollutants, absence of sulfur, and complete combustion due to the presence of a higher amount of free oxygen (Folayan et al., 2019). There are several techniques for obtaining biodiesel from different raw materials, including pyrolysis or thermal cracking, microemulsion, direct blending, and transesterification (Kayode and Hart, 2019). Among these, transesterification is the simplest and most practical method for biofuel production, which is why it is the most widely used technique at the industrial level (Mofijur et al., 2021). On the other hand, value-added products derived from vegetable oils, such as biolubricants, can be obtained through methods such as hydroxylation, esterification, epoxidation, and transesterification.

Similarly, transesterification is the most used technique, as it can be integrated as a second stage within the biodiesel production process (Encinar et al., 2020). Transesterification for biodiesel production involves the reaction of triglycerides with short-chain alcohols, such as methanol, in the presence of a catalyst to form alkyl esters and glycerol as a byproduct, whereas transesterification for biolubricant production involves a reaction in which one ester is transformed into another ester through the exchange of an alkyl group provided by a higher alcohol, on which the complexity of the final product depends (Mofijur et al., 2021). Some of the key factors influencing both transesterification processes are the type and amount of catalyst, as well as the lipid source (Encinar et al., 2020).

In general, the catalysts that can be used are chemical and enzymatic; among the chemical ones, there are heterogeneous and homogeneous catalysts. Of these, homogeneous catalysts are more sought after because the reactions are faster and require smaller amounts (Singh et al., 2020). The main disadvantage of homogeneous catalysts is the complicated separation process, as they are in the same phase as the reaction medium, which limits their reuse (Rizwanul et al., 2020). In contrast, heterogeneous catalysts are attractive due to the efficiency with which they can be recovered through centrifugation or filtration, making their use possible in multiple catalytic cycles (Goldsmith et al., 2018). However, these separation methods require additional investment in time, energy, and money. Therefore, one alternative to improve this process is the use of materials with magnetic properties, allowing efficient removal through the application of a magnetic field (Orozco-Henao et al., 2024). Nevertheless, one drawback of magnetic catalysts is their instability against oxidation, which negatively affects both their catalytic and magnetic properties, drastically reducing their performance (Pincella et al., 2024). Kaman et al. (2024) and Rabbi et al. (2024) report that one way to improve the

stability of magnetic particles in the materials is by coating them with surfactants, polymers, or even by using chelating agents such as ethylenediaminetetraacetic acid (EDTA) (Srivastava et al., 2025). The latter acts as a ligand by binding to iron ions, enabling the formation of stable complexes of this metal (Wang et al., 2024).

In this sense, considering the manufacture of cost-effective materials, a promising option is the preparation of heterogeneous catalysts using supports derived from lignocellulosic materials and residual biomass, physically and/or chemically modified to provide suitable catalytic properties and facilitate their separation (Dhakshinamoorthy et al., 2021). Some materials reported in the literature for catalyst production include eggshells, orange, coconut, and rice peels, sugarcane bagasse, açai seeds, as well as bovine and poultry bones (Balajii and Niju, 2020; Araujo et al., 2021; Ye et al., 2024).

To obtain carbon-based supports from biomass and waste, different methods are used, such as torrefaction, liquefaction, gasification, pyrolysis, and hydrothermal carbonization (Kumar et al., 2023). Pyrolysis is one of the most used methods for obtaining biochar, generally through slow heating in an inert atmosphere at high temperatures (Clohessy and Kwapinski, 2020), whereas hydrothermal carbonization is a more environmentally friendly process as it uses lower temperatures, between 180 and 250 °C, although the carbonization time is generally longer (Abdullah et al., 2021).

Under this scenario, in the present work, cellulose acetate from cigarette filter waste was used to obtain carbon-based magnetic catalysts through hydrothermal carbonization and pyrolysis processes, to be applied in the production of biodiesel and biolubricant via the transesterification method. Cellulose acetate was used because it is a non-biodegradable and highly abundant polymer that represents a serious environmental problem, as once it fulfills its function as a cigarette filter, it is discarded on the ground, contaminating the soil and aquifers through the release and leaching of its toxic and hazardous substances (Kurmus and Mohajerani, 2020).

1.2. Hypothesis

The hypotheses of the present study were:

- a. Cigarette filter waste is an appropriate, economical, and abundant raw material to be used as support for heterogeneous catalysts applied in the transesterification of vegetable oil and alkyl esters for biodiesel and biolubricant production.
- b. The modification of carbon-based supports by impregnation with iron oxide gives catalytic and magnetic properties, which enhances the efficiency of the transesterification process and allows for efficient catalyst recovery through the application of an external magnetic field.

- c. The incorporation of chelating agents, such as EDTA, during the preparation of the materials contributes to preserving their catalytic and magnetic properties, thereby extending their useful life.
- d. The use of the magnetic properties of the catalysts facilitates their recovery and reuse in multiple catalytic cycles.

1.3. Objective

1.3.1 General objective

To prepare magnetic materials from cigarette filter waste through different synthesis routes and evaluate them as heterogeneous catalysts in the transesterification of vegetable oil and esters to produce biodiesel and biolubricant, respectively.

1.3.2 Specific objectives

- a. To develop magnetic heterogeneous catalysts by utilizing cigarette filter waste and modifying them with iron oxide through different preparation routes.
- b. To evaluate the impact of the catalyst preparation route on their catalytic performance to produce biodiesel and biolubricant.
- c. To evaluate the influence of EDTA on the preservation of the catalytic and magnetic properties of the materials.
- d. To determine the optimal reaction conditions to produce biodiesel and biolubricant.
- e. To obtain the transesterification kinetics and kinetic parameters to produce biodiesel and biolubricant using the best evaluated catalysts, through the modeling of experimental data.
- f. To characterize the physicochemical properties of the heterogeneous catalysts at different stages of preparation.
- g. To implement regeneration processes for the best catalysts to evaluate their reuse.

1.4. Justification

One of the primary objectives in the production of biodiesel and biolubricant through the transesterification technique is the development of efficient catalysts to ensure good yield and lower production costs (Mofijur et al., 2021). In recent years, heterogeneous catalysts have gained importance due to the ease with which they can be recovered and, therefore, reused (Goldsmith et al., 2018). Another advantage of this type of catalyst is that they can be prepared using supports derived from economical and abundant raw materials (Dhakshinamoorthy et al., 2021). In this regard, cigarette filter waste is a possible option for obtaining materials applied in catalytic transesterification to produce biodiesel and some value-added products, aiming to make use of these wastes that lack official disposal methods.

Currently, cigarette filter waste is one of the most abundant types of litter, with over 800 thousand tons per year, and its problem lies in its composition, since it is made of cellulose acetate fibers, a non-biodegradable polymer, which only undergoes slow and partial photodegradation (Wang et al., 2020; Belzagui et al., 2021). The main issue is the lack of proper control of this waste, as once their function is finished and given their small size, consumers easily dispose of them by throwing them on the ground. In Mexico alone, the average number of cigarettes consumed per smoker is 7.4 per day, and currently, the number of smokers is around 15.6 million (Ibarra-Salazar et al., 2020). Once in the soil or even in water, their substances easily leach or dissolve, contaminating these environments mainly with lead, cyanide, arsenic, and mercury, becoming a source of toxicity for organisms (Kurmus and Mohajerani, 2020).

The filters that are collected can be eliminated by incineration or landfilling; however, these are not adequate methods since they are neither economically nor environmentally viable, as there is a possibility of contaminant leakage into groundwater and the atmosphere (Torkashvand et al., 2020). Furthermore, the application of cigarette filter waste would be in one of the current areas of interest: the production and application of clean and environmentally friendly energy sources, due to the intensive supply of petroleum having led to a decrease in its reserves and concerning environmental pollution (Martins et al., 2019).

Additionally, one of the main challenges in obtaining these products is the use of catalysts that can be reused to reduce production costs. Therefore, the incorporation of magnetite into catalytic materials is an alternative to improve their recovery, facilitating their reuse in multiple reaction cycles.

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Chapter 2. Theoretical foundations

2.1 Energy sources

Throughout history, humans have used energy from various sources, both renewable and non-renewable (see Figure 2.1), which has become an essential resource for the development of countries in the social, industrial, and economic spheres (Dilanchiev et al., 2024).

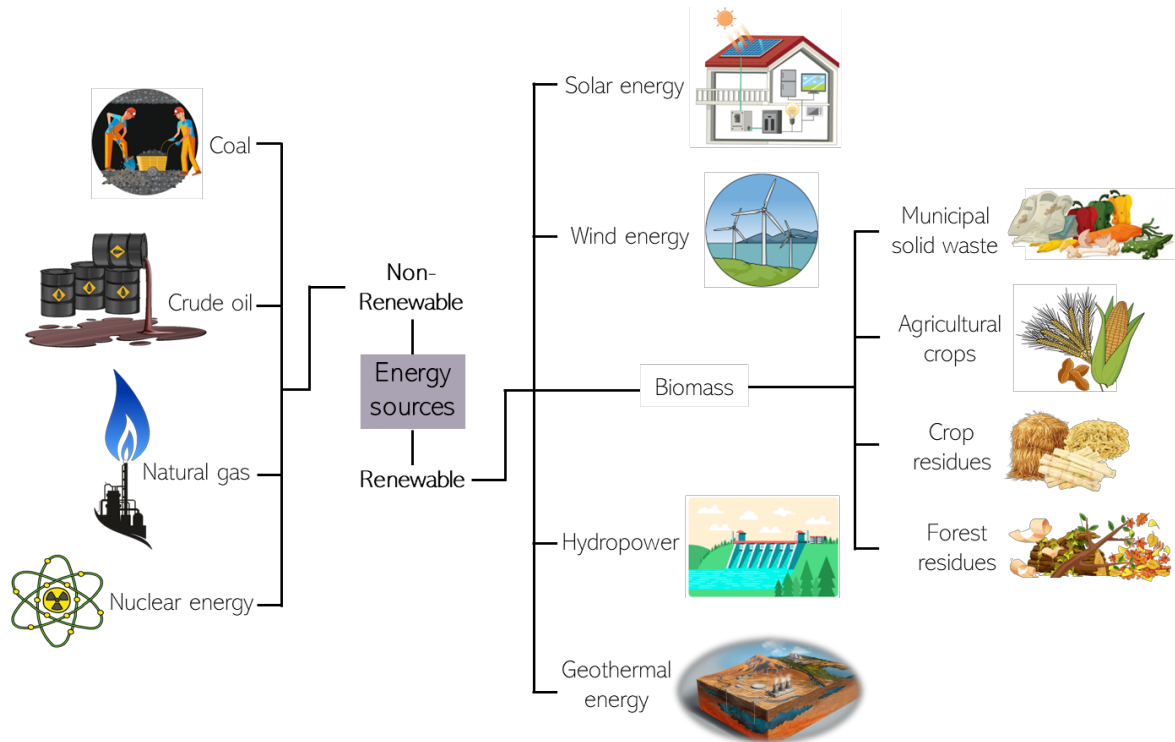


Figure 2.1 Renewable and non-renewable energy sources

Non-renewable energy sources include conventional fuels, also known as fossil fuels, such as oil, coal, and gas, which account for up to 85% of global energy demand (Owebor et al., 2025). This classification also includes nuclear energy, although it only contributes to approximately 4% of the energy used (Peng et al., 2020). These sources are characterized by being highly efficient due to their high energy density, which facilitates the transportation and storage of large amounts of energy in small volumes, which is why they have dominated the transportation sector, which consumes up to 60% of the total energy produced (Pramuanjaroenkij and Kakaç, 2023). However, these sources have serious disadvantages, such as non-renewability, environmental pollution, and the generation of high CO₂ emissions (Zaghdoudi et al., 2024). This not only contributes to global warming, but also affects people's health, causing around 4.2 million deaths per year due to heart disease, stroke, lung cancer, and chronic diseases, as approximately 91% of the population lives in areas that exceed air quality standards (McKinney, 2019).

Although nuclear energy has helped reduce fossil fuel consumption and lower carbon dioxide emissions, the management of its waste and the accelerated aging of reactors are drawbacks of using this resource (Bersano et al., 2020). That is how the energy demand, the decrease in fossil resource supply, and climate change have increased the need for alternative, renewable, and sustainable energy sources (Raud et al., 2019; Suparmaniam et al., 2019).

Renewable energy sources are derived from natural resources that can be replenished continuously and quickly in comparison to non-renewable sources (Magazino et al., 2021). Additionally, they are cleaner and more abundant sources, which represents an opportunity to decrease dependence on fossil fuels and, with that, mitigate the negative impact on the environment (Akusta and Cergibozan, 2026). Renewable energy sources include solar, wind, hydroelectric, geothermal, and biomass (Zhdaneev et al., 2024).

Within renewable energy production, biomass (any organic matter of plant origin) and waste (materials generated at the municipal and industrial level) account for more than 70%, with direct combustion being the most common use (Proskurina et al., 2018; Raud et al., 2019). However, in recent years, these materials have gained relevance as a source with the ability to be transformed into a wide variety of energy products, through thermochemical and biochemical technologies and processes (Ong et al., 2019). Among these products are biogas and liquid biofuels (biodiesel and bioalcohol), as well as biolubricants, which are widely used in the transportation sector (Ao et al., 2024; Rosas-Medellín et al., 2025). One of the main advantages of biomass is that it comes from agricultural, forestry, industrial, and other unconventional waste, making it a cheap and easily accessible raw material (Ashmath et al., 2025; Khandaker et al., 2025). In this sense, the use of renewable sources for the development of clean technologies is a key point for achieving a more sustainable energy model.

2.2 Biodiesel

Biodiesel is a liquid fuel obtained from renewable raw materials, produced chemically through a catalyzed reaction of lipids (animal fat or vegetable oil) with an alcohol, whose product is composed of alkyl esters of fatty acids, which makes it non-toxic and easily available (Neupane, 2023).

Its importance lies in the fact that it represents a promising energy alternative for reducing air pollution generated by the transportation sector, as it can be used in diesel engines, even without modifications, which are widely used in trucks and commercial vehicles (El-Sheekh et al., 2023). The operation of these engines produces fewer hydrocarbon and carbon monoxide emissions compared to gasoline engines, although it generates a greater amount of nitrogen oxide and particulate matter (Cong et al., 2017). In this sense, replacing conventional diesel with biodiesel, or using a mixture of both, is an effective alternative to mitigate the release of harmful gases and particles (Kharia et al.,

2023). This is because biodiesel is a green, renewable fuel with almost zero sulfur and aromatic compound content, which prevents the emission of hazardous pollutants (Shirmeshan et al., 2025). Its emissions are reduced to almost carbon dioxide, which can be absorbed by plants thanks to its photosynthetic origin, making it a carbon-neutral biofuel capable of significantly reducing the greenhouse effect and global warming (Mondal et al., 2023). Furthermore, it contains approximately 11% incorporated oxygen, which promotes complete combustion (Liu et al., 2021).

2.2.1 Properties of biodiesel

The incorporation of biodiesel into the transportation sector has been possible because it shares several physicochemical properties with fossil diesel (see Table 2.1). However, the chemical composition of these two fuels is different, as diesel is made up of straight-chain hydrocarbons (12 and 24 carbons), while biodiesel is composed of alkyl esters of fatty acids, as mentioned earlier (Wu et al., 2020). These esters vary depending on the lipid source used, which in turn determines the properties of the biofuel.

Table 2.1 Physicochemical properties of biodiesel and fossil diesel

Property	Fuel	
	Biodiesel	Fossil diesel
Density, kg/m ³	860 – 900	820 – 845
Cetane number	≥ 51	≥ 51
Flash point, °C	120	55
Kinematic viscosity, mm ² /s	1.9 – 6.0	1.9 – 4.1
Calorific value, MJ/kg	37 – 40	42 – 46
Oxidation stability, h	≥ 8	> 20

• Density

Density is one of the fuel properties that directly affects engine performance and combustion quality (Vasileiadis et al., 2025). Density depends on the chemical structure of the fatty acids present in each type of oil and therefore on the molecular mass of the esters produced during the reaction of the lipid source with the alcohol, although density generally ranges from 832 kg/m³, as in the case of biodiesel derived from beef tallow and jojoba oil, to 928.5 kg/m³, as in the case of biodiesel derived from castor oil (Rahman et al., 2021). In general, the density of biodiesel is higher than that of conventional diesel (820-845 kg/m³), which improves the quality of the fuel, whose ideal range is between 860 and 900 kg/m³ (Osman and Stefaniu, 2023).

• Kinematic viscosity

Viscosity is also an important property that determines fuel quality and efficiency, as lower viscosity facilitates the atomization process during injection, promoting the formation of finer

droplets and, therefore, more complete combustion with less particle deposition (Wu et al., 2020). Although biodiesel viscosity can be up to twice that of diesel, this does not compromise its good performance in engines. The direct use of vegetable oils as fuel has even been considered, however, their viscosity is up to ten times greater than that of biodiesel, which represents a significant challenge for its application without prior processing (Ramírez-Verduzco and Hernández-Sánchez, 2024).

- **Cetane number**

Cetane number is a parameter used to determine the time that elapses between the injection of the fuel and the start of combustion. A high value indicates that the fuel ignites more easily when mixed with high-pressure compressed air, resulting in a lower ignition delay (Lin and Wu, 2022). The cetane number of both biodiesel and diesel must be at least 51 to ensure good engine performance and clean, efficient combustion, according to European standards EN 14214 and EN 590.

- **Flash point**

The flash point of fuels is a fundamental property of fuels, as it allows estimating their level of flammability and volatility. This feature is essential for assessing fire or explosion risks during various stages such as production, storage, and transportation, facilitating the identification of substances with high potential for danger (Semorile et al., 2023). In technical terms, the flash point refers to the minimum temperature at which the fuel emits vapors capable of igniting upon contact with an ignition source (do Nascimento et al., 2021). The flash point depends on the chemical composition of the biodiesel, but its value, which must be at least 120 °C according to European standards, is also affected by the presence of unreacted alcohol (Rahman et al., 2021).

- **Calorific value**

The energy content of a fuel is defined as the amount of energy released when a specific volume of the fuel is completely burned. Generally, this value is sought to be high, as greater heat release during combustion contributes to optimizing engine performance (Shehab et al., 2022). However, compared to conventional diesel, biodiesel has a lower calorific value, which is mainly attributed to the oxygen chemically incorporated into its molecular structure (Rahman et al., 2021).

- **Oxidation stability**

Fuels must have excellent oxidative stability to prevent the formation of gums, acids, and sediments that accumulate in the components of the combustion system, affecting the performance and durability of the engine (Varghese et al., 2021). Like the rest of the properties, oxidative stability is closely related to the composition of its fatty acids, being more vulnerable when the degree of unsaturation is higher (Lei et al., 2024). Therefore, oxidative stability refers to the ability of fuel to maintain its chemical structure during storage without undergoing significant alterations (Masudi et

al., 2023). Although biodiesel has a disadvantage compared to petroleum-derived diesel in terms of lower oxidation resistance, this can be delayed by adding antioxidant agents (Varghese et al., 2021).

2.2.2 Raw materials used in biodiesel production

Biodiesel can be obtained from a lipid source such as pure or used vegetable oils, animal fats, and oils of microbial origin, whose fatty acids are commonly transesterified with an alcohol in the presence of a catalyst. In addition to fatty acid alkyl esters, glycerol is also obtained as a by-product (Zhang et al., 2020). The raw material used in the production of biofuels significantly influences the physicochemical characteristics, since the composition and purity vary depending on the oil or fat used, also affecting the yield and production cost (Go et al., 2016).

Moreover, according to the raw material used, biodiesel is classified into one of the four already established generations (see Figure 2.2) (Mahdavi et al., 2015).

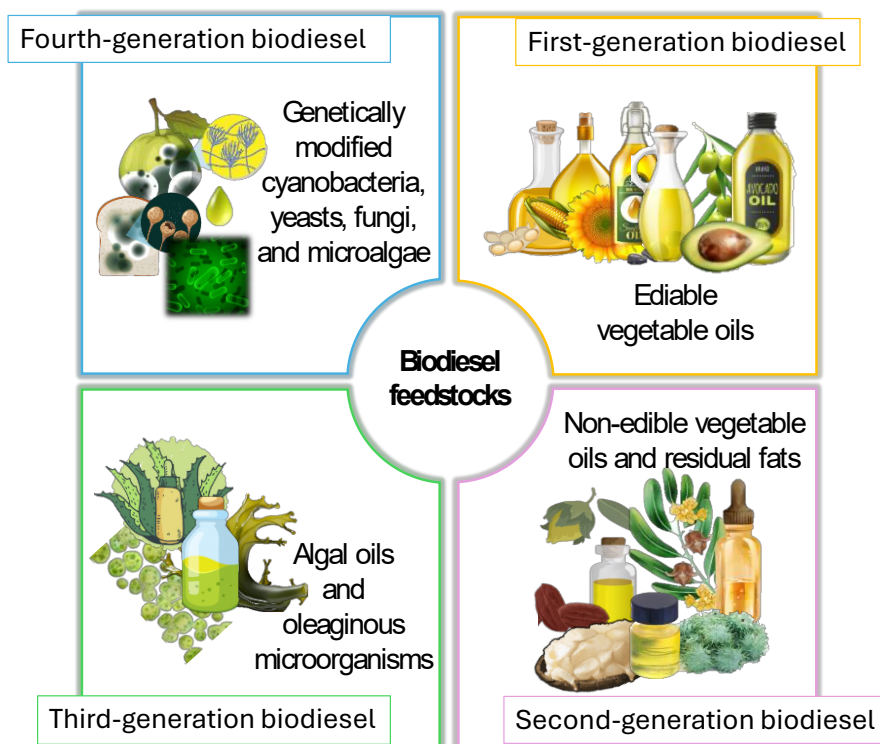


Figure 2.2 Biodiesel classification according to lipid feedstocks

First-generation biodiesel is produced from vegetable oils obtained from edible biomass such as soybean, peanut, coconut, sunflower, corn, among others (Brännström et al., 2018). Initially, these types of oils were widely used in biofuel production since they are easy to extract and, being pure, require no treatment for acidity or moisture content. However, they directly compete with food products and agricultural land, increasing their cost (Uyamaz, 2018).

The raw material for second-generation biodiesel is more affordable compared to first-generation biodiesel, as it does not compete with food products. It is obtained from non-edible lignocellulosic material such as rice and wheat straw, corn stalks, pine wood, *Jatropha* or *Karanja* seed oil, as well as animal fats or used cooking oils. However, they require a larger amount of alcohol in the transesterification process (Patel et al., 2019; Singh et al., 2020).

Third-generation fuels are obtained from algal oils and oleaginous microorganisms (microalgae), whose main advantages include low competition for farmland, high yield, and year-round production. However, the production cost is high due to the complex technology required (Mofijur et al., 2019; Foteinis et al., 2020).

Finally, fourth-generation biodiesel is obtained from genetically modified cyanobacteria, yeasts, fungi, and microalgae, which can capture and convert atmospheric carbon dioxide into fuel using solar energy and artificial photosynthesis (Huang et al., 2020).

2.2.3 Biodiesel production techniques

The conventional processes used for obtaining biofuels from lipid sources are divided into physical and chemical methods, according to the processing technique and the characteristics of the final product (Cong et al., 2017). Physical methods are subdivided into the direct blending method and the microemulsion method, while chemical methods include pyrolysis and transesterification (Velusamy et al., 2021).

The direct blending method consists of using the oils directly by mixing or diluting them with diesel, making the method low-cost and highly thermally efficient. However, it results in high density, high viscosity, and low volatility, which negatively affects engine combustion performance due to poor atomization and injector nozzle clogging, increasing corrosion and reducing engine lifespan (Aransiola et al., 2014).

Lipid feedstock can be treated with the microemulsion method to obtain a fuel with low viscosity and high volatility. This method is characterized by a simple and direct reduction in viscosity by adding solvents or surfactants. However, problems arise after prolonged use of this fuel, as it increases carbon deposits and the viscosity of lubricating oils, and combustion is incomplete (Velusamy et al., 2021).

Pyrolysis, on the other hand, is a method that breaks down plant or animal feedstocks into alkanes, olefins, dienes, aromatics, and carboxylic acids by applying high temperatures with or without the presence of a catalyst and in the absence of oxygen to prevent oil oxidation, yielding a biofuel like diesel. However, it has not been favored due to its high cost, low conversion rate, and high energy consumption (Quah et al., 2019).

Transesterification is the main method for biodiesel production, in which vegetable oils or animal fats and short-chain alcohols are subjected to a reaction in the presence of a chemical or enzymatic catalyst, with the chemical catalyst (homogeneous or heterogeneous) being the most used (Mandari and Kumar, 2022). Transesterification is the most widely used technique due to its advantages over other production methods, such as the use of a variety of raw materials. It improves fuel properties by reducing its viscosity, allowing miscibility with any proportion of fossil fuel, and it is cost-effective and shows high conversion efficiency (Velusamy et al., 2021). Additionally, glycerol, a high-value chemical, is obtained as a by-product (Vivek et al., 2017).

2.2.4 Emerging transesterification techniques

Although conventional transesterification is the most used technique due to its multiple advantages, it has certain limitations that have been addressed with the introduction of technologies such as ultrasound, microwave application, reactive distillation, membrane technology, the non-catalytic supercritical method, and the biox process (Kayode and Hart, 2019).

Ultrasonication enhances mixing, heat, and mass transfer due to the generation of cavitation bubbles produced by sound waves, reducing reaction time and energy consumption. It also yields higher output and better-quality glycerol as a by-product. However, its drawback is the undesirable formation of soap and, consequently, the generation of wastewater due to the washing of the product (Tan et al., 2019).

Microwave application also aims to reduce reaction time, making it up to 10 times shorter than with conventional transesterification. This is due to overheating caused by the collision and friction between moving molecules due to the oscillation of their polar ends. However, it is not suitable for industrial use due to microwave leakage and high energy consumption (Maleki et al., 2024).

Reactive distillation facilitates the separation of the components involved in the reaction by integrating chemical reaction and distillation into a continuous process, reducing alcohol consumption by up to 66% and increasing conversion. The drawback of this technique is that the reboiler and condenser significantly increase capital investment and operating costs (Tan et al., 2019).

Membrane-based transesterification integrates reaction and separation into a single step by taking advantage of the immiscibility of methanol and oil, thus preventing the formation of side reactions and producing FAME-rich products. However, it requires high manufacturing costs because it needs membranes with special characteristics, which are expensive (Lee et al., 2025).

The supercritical method has the advantage of achieving almost complete conversion in a relatively short time and does not require a catalyst. With the use of high temperatures and pressures, up to 400 °C and 295 atmospheres, it achieves miscibility between alcohol and triglycerides, accelerating the reaction and avoiding problems related to catalyst deactivation, separation from the

mixture, and wastewater generation. However, it is an unfeasible and uneconomical process due to its high energy demand and the high methanol requirement (Tan et al., 2019).

The biox process is another non-catalytic method in which co-solvents are used to solubilize methanol, generating a monophasic system and thus reducing reaction time. This process is suitable for raw materials with high free fatty acid content (Srivastava and Gaurav, 2019). The most used co-solvent is tetrahydrofuran, which has a boiling point like methanol, making its separation from the product difficult and compromising compliance with biofuel standards (Tan et al., 2019).

2.2.5 Parameters affecting biodiesel production using conventional transesterification techniques

Although emerging transesterification technologies offer great advantages, such as reduced reaction time, they present significant drawbacks, especially in terms of cost and energy consumption. Therefore, conventional transesterification remains the most widely used method in the industry, as it is a simple process that yields high outputs without requiring special equipment, unlike some of the technologies mentioned above (Mofijur et al., 2021). However, there are several parameters that influence the transesterification process. Some of them depend on the reaction conditions and must be optimized to achieve an efficient process with high yields and products that meet the standards' specifications. The most significant factors include free fatty acid and water content, type of alcohol, molar ratio used, type and concentration of catalyst, temperature and duration of the reaction, and stirring speed (Ajala et al., 2020).

- **Free fatty acid content**

The composition of the fatty acids in the raw material influences the final properties of the biofuel, as it determines the structure of the formed fatty acid esters, which in turn affect the cetane number, oxidative stability, and iodine value (Akubude et al., 2019). Additionally, the raw material must be of good quality, since a high content of free fatty acids and moisture leads to soap formation and therefore to low yield and high production costs (Ajala et al., 2020).

- **Alcohol**

The alcohol used in biodiesel production through transesterification may contain up to 8 carbon atoms; however, short-chain alcohols are preferred due to better conversion performance. Methanol is the most used alcohol because of its lower cost, greater availability, and superior reactivity (Ajala et al., 2020).

- **Oil/alcohol molar ratio**

The alcohol-to-oil ratio is one of the factors that affect the formation rate and yield of FAME. Theoretically, the molar ratio is 3:1, but since the reaction is reversible, an excess of alcohol is required to drive the transesterification toward biofuel production. Therefore, a low molar ratio will

reduce triglyceride conversion, whereas a ratio that is too high may also lower the yield due to emulsification between products caused by the OH group of the alcohol (Chozhavendhan et al., 2020).

- **Type and concentration of catalyst**

The catalyst is crucial, as it accelerates the reaction rate. Additionally, its appropriate concentration must be determined to ensure optimal conversion without increasing the viscosity of the mixture due to emulsion formation when overdosed (Verma & Sharma, 2016). Catalysts used in transesterification may be chemical (homogeneous or heterogeneous) or enzymatic, whose advantages and disadvantages are shown in Table 2.2.

- **Temperature**

The selected temperature in the transesterification process will depend on the catalyst and the raw material used. It affects product yield and reaction time, as increasing the temperature decreases the viscosity of the fatty acids, improving mixing and thereby accelerating the reaction. However, excessively high temperatures may lead to secondary reactions, decreasing yield (Verma & Sharma, 2016)

- **Reaction time**

The transesterification reaction may last from minutes to hours, depending on the temperature, reaction rate, type of catalyst, and raw material used. Nevertheless, total oil consumption is achieved with longer reaction times (Singh et al., 2020).

- **Stirring speed**

Stirring speed affects the mixing of the oil or fat, alcohol, and catalyst, facilitating molecular collisions and improving mass transfer. If the stirring speed is not adequate, product yield may decrease, or soap formation may be favored if the speed is too high (Chozhavendhan et al., 2020).

2.2.6 Use of heterogeneous catalysts

Due to the advantages shown by heterogeneous catalysts, they have been preferred in transesterification, mainly due to their ease of recovery from the reaction medium, allowing reuse in several catalytic cycles (Goldsmith et al., 2018).

Therefore, researchers have focused their attention on preparing catalytic materials that are environmentally friendly and manufactured from lignocellulosic, non-lignocellulosic, and lignin-based biomass to obtain economical and reusable catalysts (Mofijur et al., 2021).

The selected biomass for material preparation is subjected to specific processes to obtain a stable carbon-based material, which is subsequently or simultaneously modified to provide it with the necessary properties to act as a catalyst. These processes include torrefaction, pyrolysis, hydrothermal carbonization, hydrothermal liquefaction, and gasification (Velusamy et al., 2021). Some of the wastes or biomasses reported in the literature include orange peels, eggshells, walnut shells, rice

husks, Jatropha seed husks, mollusk and shrimp shells, which have been treated and modified by adding a chemical compound to impart catalytic properties. These modifiers include potassium or sodium hydroxide, sulfuric acid, metal oxides, among others (Marwaha et al., 2018; Mansir et al., 2018).

Table 2.2 Advantages and disadvantages of different types of catalysts

<i>Type of catalyst</i>	<i>Examples</i>	<i>Advantages</i>	<i>Disadvantages</i>
Homogeneous acid catalyst (Singh et al., 2020)	H ₂ SO ₄ , HCl, acetates of Pb, Zn, Mn, Cd	High biodiesel yield, insensitive to free fatty acid content, simultaneous esterification and transesterification reaction, lower energy consumption.	Causes corrosion of equipment, increased production of glycerol, and difficult separation.
Homogeneous basic catalyst (Rizwanul et al., 2020)	NaOH, KOH, alkali metal alkoxides	The reaction is completed faster, they are inexpensive and widely available.	Production is affected by the content of free fatty acids causing saponification, which is difficult to recover.
Heterogeneous acid catalyst (Verma and Sharma, 2016)	Metal phosphates, Zr, Sn oxides, sulfonated mesoporous silicas	They are easily separated from the reaction mixture, insensitive to the free fatty acid content, used in low-quality raw materials, and can be reused.	It requires a high reaction temperature, a higher molar ratio and a long reaction time.
Heterogeneous basic catalyst (Goldsmith et al., 2018)	K ₂ CO ₃ , CaO, BaO, Ba(OH) ₂	Easy to separate from the reaction mixture, low waste generation, can be regenerated and reused.	A high content of free fatty acids causes saponification, complicating the purification process and reducing the yield.
Enzymes (Ferreira et al., 2019)	Lipases	Suitable for low-quality raw materials, as they are insensitive to free fatty acids and water content. They use low temperatures and produce high-purity products.	Relatively low performance, long reaction times, they are expensive.

2.3 Biolubricants

Lubricants are mineral oils widely used in any mechanical system, with the purpose of reducing wear and friction between surfaces and moving parts due to the formation of a film that helps prolong equipment life and improve process efficiency. Therefore, their use is essential to ensure proper, continuous, and above all, cost-effective operation (Mobarak et al., 2014; Almasi et al., 2021). Approximately 95% of lubricants are obtained from crude oil distillation, including transmission oils, compressor oils, metalworking fluids, and hydraulic oils (Encinar et al., 2020). In addition to reducing

surface wear, lubricants protect against corrosion, reduce oxidation, prevent heat loss resulting from contact between moving surfaces, particularly in engines and drive trains, and act as insulators and sealing agents against dirt, dust, and water (Mobarak et al., 2014; Sing et al., 2017).

The main problems with lubricants derived from fossil resources are their limited production due to oil availability and the environmental damage caused by direct contact with soil or water after disposal. It is estimated that between 50% and 75% of lubricants enter the environment, and globally, annual production reaches 40 million tons (Almasi et al., 2021). Moreover, the emission of trace metals such as calcium, phosphorus, zinc, magnesium, and iron nanoparticles due to combustion has been reported (Mobarak et al., 2014).

Petroleum-based lubricants are composed of paraffinic hydrocarbons (linear/branched), olefinic, naphthenic, and aromatic hydrocarbons with 20 to 50 carbon atoms, which are toxic (Cecilia et al., 2020). An alternative to these lubricants is the use of vegetable oils or animal fats, as they are composed of triglycerides, which possess excellent lubricating power, a high viscosity index, wear resistance, renewability, and are 90–98% biodegradable (Cermak et al., 2018). However, they also exhibit low oxidative stability and a high pour point, which limits their direct use as lubricants (Sukirno & Rahadi, 2020). Therefore, the production of biolubricants through the chemical modification of triglycerides is a promising option to improve those aspects that limit their application. Moreover, they show excellent biodegradability and low toxicity, decomposing rapidly in soil without affecting organisms (Owuna et al., 2020).

2.3.1 Chemical reaction of triglycerides to produce biolubricants

As mentioned previously, triglycerides can be used directly as lubricants since they form a strong film between surfaces, reducing wear and friction. However, they react rapidly with oxygen in the air, leading to the sedimentation of insoluble materials, increased acidity, and higher viscosity, issues that can be prevented through chemical modification to improve their physicochemical properties by converting them into more stable molecules (Edla et al., 2023).

The chemical modification methods used to correct acyl (C=O), alkoxy (O-R), and C=C double bond functional groups include hydrolysis and estolide formation, hydroesterification, epoxidation followed by ring opening, and acetylation, as well as esterification/transesterification, the latter two being the most used techniques (Almasi et al., 2021).

• Estolide formation

Estolides, a new class of esters, are formed through the reaction between a carboxylic group and the C=C double bond of fatty acid molecules, which may vary in chain length and unsaturation and can be obtained from inexpensive lipid sources (Almasi et al., 2021). Estolides (oligomeric fatty acids) are synthesized through the application of acid catalysts (see Figure 2.3), such as sulfuric acid

or perchloric acid (De Haro et al., 2018). Compared to triglycerides, estolides have greater hydrolytic resistance due to their secondary ester bonds (Hoong et al., 2020).

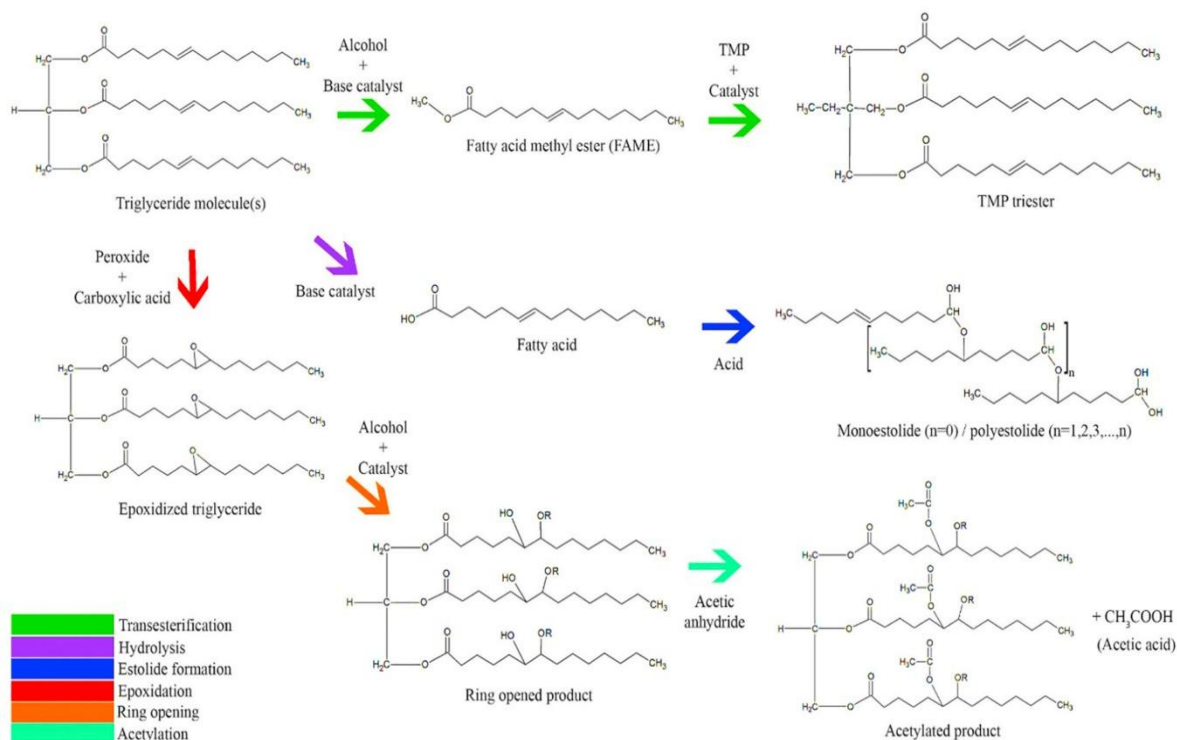


Figure 2.3 Chemical modification of triglycerides through different routes (Almasi et al., 2021)

• Hydroesterification

Hydroesterification consists of a sequential hydrolysis of triglycerides to obtain free fatty acids, which are then esterified with different alcohols in the presence of catalysts, as shown in Figure 2.4 (Bolina et al., 2021). The advantage of this technique is the variety of raw materials that can be used, including animal fats, non-edible oils, and waste cooking oils, as the presence of high levels of free fatty acids and water is not an issue (Pedroza et al., 2019; Bolina et al., 2021). However, only acid catalysts can be used to avoid soap formation that would occur with alkaline catalysts (Takase and Essandoh, 2020).

• Epoxidation, Oxirane Ring Opening, and Acetylation

The main objective of the epoxidation process is to correct C=C double bonds, as these are responsible for promoting oil oxidation, leading to the formation of peroxides, polymerization, and hydrolytic degradation (Almasi et al., 2021). Epoxidation consists of the formation of oxirane rings through the reaction between fatty acids and a peracid, which is obtained from the reaction between hydrogen peroxide and carboxylic acid such as acetic or formic acid (Freites et al., 2018). Therefore, initially, the carboxylic acid reacts with the peroxide in the aqueous phase, and in a second step, the

- **Transesterification**

Transesterification is a chemical reaction in which one ester is converted into another by exchanging the alkyl group of alcohol (Mandari and Kumar, 2022). The production of biolubricants can occur in a single reaction step between triglycerides and alcohols or in two successive transesterification stages (Bolina et al., 2021). In the first stage, triglycerides are converted into ethyl or methyl esters by using short-chain alcohols, while in the second stage, higher alcohols are used, which react with the esters formed in the first step (Almasi et al., 2021).

Double transesterification yields many valuable products and by-products, making this process highly economical since most of the by-products can be reused in the process or even marketed. Therefore, this production route can be appropriately implemented in biorefineries, with advantages such as the use of natural and renewable sources, the production of valuable products like biodiesel and biolubricants, the reuse of by-products such as methanol, and the generation of marketable by-products like glycerol, which has a wide range of uses depending on its purity (Encinar et al., 2021).

Like transesterification for biodiesel production, the efficiency of biolubricant production and their properties are influenced by various factors, including the lipid source, catalyst, and alcohol (Uppar et al., 2023). Among them, the type of alcohol used in this process plays a decisive role, as its long or branched chain influences viscosity, thermal and oxidative stability, as well as volatility, which are essential characteristics for the use of the esters obtained as lubricants (Nogales-Delgado et al., 2023).

The most commonly used long-chain or branched higher alcohols include butanol, isobutanol, 2-ethylhexanol, and various polyols such as ethylene glycol, trimethylolpropane, and pentaerythritol (Encinar et al., 2022). In particular, the branched structure of alcohol improves the lubricant behavior at low temperatures because it reduces its fluidity point and the tendency to crystallize (Cecilia et al., 2020). However, the choice of alcohol not only defines the efficiency of the process and the functionality of the product but also affects the selectivity and kinetics of transesterification (Encinar et al., 2020). Alcohols with low molecular weight react more easily in the presence of alkaline catalysts, while more complex alcohols require specific catalysts, as well as higher reaction times and temperatures, due to their lower reactivity and higher viscosity (Zorn et al., 2020).

The catalyst is also a decisive factor in transesterification, as its nature influences the reaction rate, the conversion of the esters, and the selectivity towards the desired products, directly affecting the quality of the bio-lubricant (Shrivastava et al., 2023). Catalysts must possess thermal and chemical stability to resist deactivation by water and other compounds that may be present in the reaction medium, and they must also have strong and accessible active sites to promote the reactivity of alcohols (Encinar et al., 2020).

When using heterogeneous catalysts, it is essential that they have a porous structure and a high surface area to facilitate the diffusion of reactants to the active sites (Masudi and Muraza, 2018). These active sites can be basic in nature (-OH, carbonates, alkali metal oxides) that promote the deprotonation of the alcohol, or acidic (-SO₃H, -COOH, Lewis acid in metal oxides) (Encinar et al., 2020). In addition to these, there are enzymatic catalysts, mainly lipases, which are highly valued for their great selectivity and because they allow working with mild reaction conditions and with lower quality raw materials; however, their high cost makes them a less attractive option (Bolina et al., 2021).

On the other hand, the use of high reaction temperatures is important due to the viscosity of the reactants and the low reactivity of higher alcohols, so the temperature range is typically between 120 and 160 °C, depending on the alcohol and the catalyst used (Hadiza et al., 2025).

2.3.2 Properties of biolubricants

Biolubricants exhibit highly valuable physicochemical properties, sometimes even better than petroleum-derived lubricants, as they feature high lubricity, high VI (viscosity index), high flash point, and lower evaporation losses during storage (Singh et al., 2017). Some of these properties are described below.

- **Viscosity**

Viscosity is a measure of the thickness of the biolubricant or its resistance to flow. The higher it is, the thicker the lubricant, and more energy is required to move an object through it. Therefore, viscosity is an important factor in determining the application of biolubricant (Owuna et al., 2020).

- **Viscosity index (VI)**

It indicates the change in viscosity with temperature fluctuations. Viscosity is inversely proportional to temperature, so a high VI indicates small viscosity changes with temperature and vice versa. A machine operating over a wide temperature range requires a lubricant with a higher VI since the higher the viscosity index, the lesser the effect of temperature on the biolubricant's viscosity (Mobarak et al., 2014).

- **Cloud point**

This is the temperature at which the first sign of cloudiness is observed. The operating temperature must be above the cloud point to avoid wax crystal formation, which could cause deposits on surfaces or clog filters and openings (Owuna et al., 2020).

- **Pour point**

The pour point is a crucial parameter for equipment operating in cold environments or handling cold fluids. It is the lowest temperature at which a biolubricant sample can flow by gravity. Thus, biolubricants with low pour points can operate at low temperatures (Singh et al., 2017).

- **Flash point and fire point**

The flash point is the lowest temperature at which a vaporized lubricant can be ignited by an external source, while the fire point is the temperature at which combustion is sustained (Owuna et al., 2020). These factors are important for transport and storage as they indicate the biolubricant's volatility and fire resistance (Singh et al., 2017).

- **Acid number**

This indicates the concentration of acidic compounds. If it is high, this must be considered in its applications, as it may cause machinery corrosion or filter clogging (Mobarak et al., 2014).

- **Oxidative stability**

This is the ability to resist oxidation formation and is used to predict the biolubricant's shelf life under extreme conditions (Owuna et al., 2020). Low oxidative stability indicates rapid oxidation, making the biolubricant thick and plastic-like due to polymerization. Therefore, one must consider the surface on which it will be used, the presence of water, and the operating temperature (Singh et al., 2017).

- **Iodine value**

The iodine value is related to oxidative stability, as it measures the amount of double bonds in the molecules of biolubricants, which are susceptible to oxidation. Therefore, a low iodine value is desirable (Mobarak et al., 2014).

2.3.3 Applications of biolubricants

Biolubricants have industrial and maintenance applications. They can be widely used in machines that, during their operations, release oil directly into the environment, as well as in machinery located in environmentally sensitive areas such as water treatment and food processing (Mobarak et al., 2014). They are generally used in hydraulic fluids, power equipment, two-stroke engines, aircraft and ship engines, as well as metalworking fluids such as chainsaw oils, drilling fluids for geological and marine explorations, railway flange lubricants, cutting fluids, transmission fluids, white oils, instrumental oils, among others (Owuna et al., 2020).

2.4 Purification of raw materials and final products

The use of quality raw materials in the production of bioenergetics is a critical point to ensure an efficient process. Additionally, it is necessary to obtain products that meet the standards established by regulations so that their application does not cause problems either in terms of energy performance or machinery malfunction due to the deposition of unwanted compounds (Singh et al., 2017).

Among the parameters evaluated in biofuels are the percentages of free and total glycerol, phosphorus and sulfur content, water content, methanol, monoglycerides, diglycerides, and

triglycerides, as well as the presence of alkali metals, which must be taken into account to preserve the stability of the biofuels, especially when they are stored for prolonged periods, since poor stability leads to increased acidity index and viscosity, as well as the formation of gums and sediments (Leung et al., 2019).

The raw material must also undergo pretreatment before being used for biofuel production. This is applied to lipid sources with a low level of purity, as is the case with used cooking oil, which contains significant amounts of free fatty acids, gums, and water resulting from the frying process (Chairul et al., 2021). Although the purification process can make biofuel production more complex, the goal of using this type of raw material is to overcome economic challenges, as it can represent up to 70% of the production cost (Leung et al., 2019).

2.4.1 Purification techniques

Raw materials may contain phospholipids, water, and free fatty acids, the latter being the most prominent and undesirable impurities due to their tendency to react and form soap (Chairul et al., 2021). The purification processes for raw materials are simpler than those for biofuels, as some impurities can be removed by filtration or centrifugation. However, others require more elaborate processes, such as extraction and distillation with organic solvents or supercritical fluids, which makes the process costly and energy-intensive (Kandel et al., 2013).

Adsorption, a process in which a material (adsorbate) accumulates on the surface of a solid (adsorbent), is a viable option for removing impurities like free fatty acids. The adsorbent can be activated carbon, MOFs, clay, or silica (Hassan et al., 2020).

Biofuels can be contaminated with the catalyst used, water, unreacted alcohol, free glycerol, and soaps, which can mainly be removed through water washing, membrane extraction, and dry washing (Leung et al., 2019).

Wet washing is done with distilled or acidified water to eliminate glycerol, alcohol, sodium salts, and residual soaps. After washing, the product is dehydrated through heat drying, vacuum flash evaporation, air bubbling, or the use of other water-absorbing agents. The main drawback of this method is the generation of wastewater, which must subsequently be properly treated, thereby increasing production costs (Veljkovic et al., 2015).

Membrane extraction removes soaps, alcohol, and glycerol through the use of porous membranes. It is an effective process because it avoids emulsification during the washing stage. However, membranes must be cleaned, and the method is inefficient at removing calcium compounds (Leung et al., 2019).

Dry washing, by applying adsorbents, is an effective process to reduce free glycerol levels and remove soaps. It is a much simpler process that does not require water, thus generating less

wastewater. It also requires less space and has low energy consumption, with the possibility of being applied in continuous processes (Veljkovic et al., 2015). Furthermore, adsorbents can be activated carbons derived from waste, making them cost-effective materials (Leung et al., 2019).

The filter, a small cylinder located at one end of the cigarette, is designed to partially or completely trap components present in the smoke to reduce the negative health impact on consumers (Qamar et al., 2020). Of the total number of cigarettes manufactured, approximately 97% have a filter composed of cellulose acetate ester (>95%), a polymer obtained by acetylation and hydrolysis of cellulose extracted from wood pulp and cotton (Andrade et al., 2019).

This polymer is characterized by being insoluble in water and by having high thermal stability and chemical resistance, properties that make it poorly biodegradable, taking up to 10 years to decompose, even with the presence of the additive titanium dioxide, a compound added during filter manufacturing to induce degradation (Putri et al., 2020).

Cigarette filters are among the most abundant waste products worldwide, irresponsibly discarded on the ground, representing a serious threat to organisms and ecosystems. These filters retain chemical components present in smoke, estimated to include up to 4,000 compounds, approximately 70 of which are carcinogenic, such as polycyclic aromatic hydrocarbons, carbon monoxide, benzene, hydrogen cyanide, phenol, ammonia, and heavy metals. Therefore, the problem with this waste, besides the prolonged time required for the filter to break down into smaller fragments is the large quantity of hazardous and toxic components that reach the soil and leach into groundwater, polluting these environments and putting the integrity of living beings at risk (Kurmus & Mohajerani, 2020).

2.5 Cigarette filter waste

Used cigarette filters, also known as cigarette butts, are a hazardous waste that could potentially be eliminated; however, as previously mentioned, the processes involved compromise the integrity of ecosystems. Therefore, alternative applications have been explored, and some uses have been reported in the literature: production of levulinic acid using the filters as a cellulose-based raw material; preparation of inorganic oxides using cellulose templates obtained through deacetylation of cellulose acetate; preparation of carbon-based catalysts for ammonia synthesis; fabrication of a sound-absorbing material; production of a material used in brick manufacturing; as a carbon source for obtaining nanomaterials used in dye detection through fluorescence; for oil absorption; and production of adsorbent materials for dye removal, among others. Thus, cigarette filter waste has the potential to be applied in various processes depending on the preparation method (Liu et al., 2015; Li et al., 2020; Lyu et al., 2021).

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Chapter 3. Recycling of cigarette filter wastes to prepare magnetic catalysts for biodiesel production: analysis of synthesis routes and catalytic properties

Abstract

This chapter reports on the valorization of cigarette filter waste to prepare new magnetic catalysts to support the energy transition via biodiesel production. Two synthesis routes have been proposed to produce the magnetic catalysts, from cigarette filter waste-derived cellulose acetate and Fe_3O_4 particles, to improve the formation of fatty acid methyl esters (FAME) from the transesterification of soybean oil with methanol. The first route involved the pyrolysis of cigarette filters and the synthesis and loading of magnetite on pyrolyzed material, while the second route included the direct use of cellulose acetate fibers and the synthesis and loading of magnetite on them. The results showed that the catalytic properties of the magnetic materials obtained from the second route outperformed those observed for the materials from the first route. The best magnetic catalyst from route 2 was utilized to perform a sensitive analysis of the transesterification conditions to maximize biodiesel production and for preliminary catalyst reuse tests. Transesterification kinetic studies were performed at 50 – 70 °C to obtain FAME formation of up to 99.5%. The rate constants and activation energy were calculated using the pseudo-first-order kinetic model under the tested operating conditions. The elemental composition, surface chemistry, and textural parameters of the catalyst and precursors were determined, analyzed, and compared. The results of this study can contribute to resolving some of the current challenges related to biodiesel production via heterogeneous transesterification using magnetic materials prepared from cigarette filter residues, which are relevant in waste management worldwide due to their environmental impact.

3.1 Introduction

Energy is fundamental for daily activities and economic development in our society (Mathew et al., 2021; Khan et al., 2023a). Fossil and renewable fuels integrate the current energy matrix worldwide (Goh et al., 2018; Johnsson et al., 2019). Despite efforts to expand the use of renewable energy, hydrocarbons continue to be a primary energy resource (Hou et al., 2023). Statistics indicate that more than 80% of the total energy demand is covered by hydrocarbons, of which > 50% is destined for the transportation sector (Malla et al., 2022).

To date, fossil fuels have been essential for technological development, but their continuous exploitation has resulted in a shortage of available reserves and a significant increase in the generation of greenhouse gases associated with climate change (Kovač et al., 2021; Tavares et al., 2021). Renewable energy is expected to play a relevant role in the coming decades only if the current technical gaps and infrastructure limitations are fully resolved to achieve the goal of generating low-cost and sustainable clean energy, including the production of liquid biofuels, such as biodiesel (Brännström et al., 2018; Zhang et al., 2022a; Thiruselvam et al., 2023).

Biodiesel is a biodegradable fuel free of aromatic compounds and sulfur, and it is composed of monoalkyl esters of long-chain fatty acids. The production of this biofuel has reduced CO₂ contribution to the atmosphere (Alsabi et al., 2024; Leite et al., 2024). It can be obtained from lipid sources (e.g., oils and fats) via different technologies, such as pyrolysis, microemulsion, or transesterification (Gotovuša et al., 2022; Aziz et al., 2023).

Transesterification is a common approach to obtain biodiesel via a reaction in which an alcohol participates in the presence of a suitable homogeneous or heterogeneous catalyst (Prasanth et al., 2021; Khan et al., 2023a). However, the transesterification process still has some drawbacks that affect the final price of biodiesel, including: a) significant water consumption for biodiesel washing (Yadav and Sharma, 2018), b) the energy consumption required to remove water from the product either by heating or vacuum application (Raheem et al., 2020), c) the cost and performance of catalysts used in the reactive system, and d) the effluent treatment of residual water generated during biodiesel washing, which may contain catalyst residues, methanol, glycerol, and other impurities (Chozhavendhan et al., 2020; Araujo et al., 2021). Consequently, the catalyst selection is a key parameter that can contribute to resolving some of these drawbacks in biodiesel production.

Chemical catalysts are a better alternative than enzyme-based catalysts, whose cost limits industrial-scale applications despite their catalytic activity and have been extensively studied to improve the performance of transesterification for biodiesel production (Gardy et al., 2019; Thangaraj et al., 2019; Kalita et al., 2022). Multiple investigations have focused on obtaining heterogeneous

catalysts from low-cost and abundant raw materials (e.g., urban and agro-industrial wastes) for their incorporation into the biodiesel supply chain (Etim et al., 2020).

The application of solid catalysts helps avoid damage to the equipment caused by corrosion associated with homogeneous reactive systems, decreases soap formation, and allows the heterogeneous catalysts to be easily recovered from the reaction medium, facilitating their reactivation and reuse (Dai et al., 2021; Hamza et al., 2021). Herein, it is convenient to indicate that the development of magnetic properties in heterogeneous catalysts allows the utilization of very low-dimensional particles, which provide a more active surface area for the catalytic process without increasing the process complexity because their separation at the end of the reaction can be performed effectively by applying a magnetic field to avoid additional filtration or centrifugation steps (Thangaraj et al., 2019; Wilkanowicz et al., 2020; Zhang et al., 2022b; Xie and Li, 2023). The use of magnetic catalysts also helps to minimize product washing, which is required to remove or neutralize the catalyst, especially in homogeneous systems. Therefore, the application of magnetic materials offers additional benefits for reducing the production cost of biofuels and avoiding the common operational problems associated with the transesterification route.

Different residues and wastes have been used for the preparation of low-cost catalysts, which have mainly focused on biomass from a variety of sources, including orange peel modified with H_2SO_4 (Lathiya et al., 2018), eggshells functionalized with Mo-Zr (Mansir et al., 2018), walnut shells treated with CaO and K_2O (Miladinović et al., 2020), turtle shell residues containing KOH (Orugba and Edomwonyi-Out, 2023), hazelnut shell ash (Miladinović et al., 2022), snail shells containing ZnO and TiO_2 (Kedir et al., 2023), animal bones (as a source of CaO) (Asaad et al., 2023), and avocado peels (Etim and Musonge, 2024). Some of these materials have been modified to confer magnetic properties on the final catalyst (Chingakham et al., 2018; Goh et al., 2021). In addition, the valorization of other rural and urban residues has been explored to obtain new materials for energy transition (Ahmed et al., 2024).

In particular, cigarette filter waste can be used as a low-cost catalyst precursor as an alternative for its valorization, helping to minimize the environmental impact caused by improper disposal. Statistics indicate that more than 800,000 tons of this residue are generated per year, as 75% of the 6 billion cigarettes that are consumed end up on the ground (Pu et al., 2019; Mghili et al., 2023; Vijayananth et al., 2024). Cigarette filters cannot biodegrade easily because their composition includes chemically stable cellulose acetate obtained from highly purified cellulose fibers (Stigler et al., 2019; Xu et al., 2019). Note that the toxic substances contained in cigarette filter residues can be easily leached and dissolved and, consequently, they are a source of toxic compounds that pollute soil and water (Qamar et al., 2020). Consequently, the preparation of novel materials to support energy

transition using this residue is a circular-economy-based contribution to waste management worldwide.

This chapter reports two preparation routes for obtaining magnetic catalysts from cigarette filter waste. The preparation conditions of the catalysts obtained from these routes were tailored to improve their performance in biodiesel production via transesterification of soybean oil, which was selected as a model reactive system. Surface characterization of the best magnetic cigarette filter-based catalyst was performed, including kinetic analysis of the tested transesterification system to obtain biodiesel.

3.2 Methodology

3.2.1 Recollection and pre-processing of cigarette filter waste

The residual cigarette filters were collected and cleaned manually. First, the coating material and impurities (e.g., ash and tobacco) were separated from the filter. The filters were bleached using a 1% w/v NaOH solution at 80 °C for 1 h (Teixeira et al., 2017). After bleaching, the samples were washed several times with deionized water at boiling temperature to remove residues trapped in the cellulose acetate fibers produced by tobacco combustion. The final filters were then dried for 4 h at 100 °C. This feedstock was utilized for the catalyst preparation.

3.2.2 Preparation routes for obtaining magnetic cigarette filter-based catalysts

The catalysts were prepared using clean and dry filters following two preparation routes, depending on the treatment applied to cellulose acetate, see Figure 3.1. Route 1 involved the preparation of a carbon-based material (CBM) via pyrolysis. Cigarette filters were pyrolyzed at 400 °C for 2 h using a Carbolite Eurotherm CFT 12165/550 tubular furnace under N₂ flow of 100 mL/min and a heating ramp of 10 °C/min (Chen et al., 2015). The CBM was divided into 3 groups: the first group was washed with deionized water, the second group was washed with 1% w/v NaOH, and the third group was not washed. All these materials were used as carbon-based support for catalyst preparation under different experimental conditions.

For the synthesis of magnetite (Fe₃O₄) supported on CBM, 0.2 g of aluminum nitrate and 1.47 g of sodium citrate were dissolved in 200 mL of 1 M NaOH at 98 °C. Immediately thereafter, a specific amount of CBM was added, and the suspension was stirred for a certain time (soaking time). NaOH acted simultaneously as a precipitating agent in Fe₃O₄ synthesis and as an activator for the formation of porous structures to facilitate Fe₃O₄ impregnation (Picasso et al., 2012; Islam et al., 2017). 20 mL of 0.5 M iron sulfate heptahydrate were added, and the mixture was allowed to react for a specific time. After the reaction, the material was recovered by magnetic attraction, dried at 100 °C for 3 h, and washed with deionized water and NaOH to remove impurities. All the samples were dried,

ground, and sieved to obtain a particle size of 0.42 mm. The synthesis conditions tested in the magnetic catalyst preparation are given by the experimental Taguchi L₉ (3⁴) array reported in Table 3.1. Four preparation variables were assessed in Route 1 to determine their impact on the catalyst properties: a) soaking time of CBM in NaOH (20 - 60 min), b) impregnation time of the carbon-based support with magnetite Fe₃O₄ (1 - 2 h), c) ratio of carbon-based support to Fe₃O₄ (0.5/1 - 1.5/1 w/w), and d) washing step of CBM (H₂O, NaOH, or no washing).

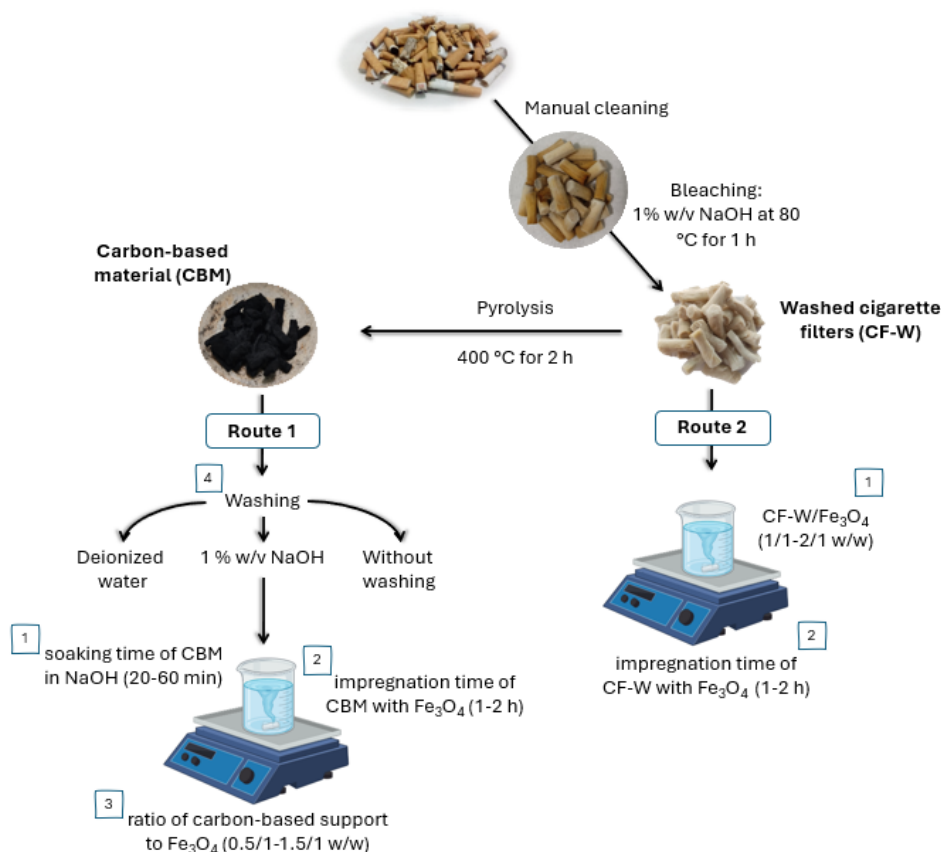


Figure 3.1 Methodology used in preparation of magnetic cigarette filter-based catalysts using Routes 1 and 2

Route 2 relied on the direct use of the cellulose acetate from washed cigarette filters (CF-W) to obtain the magnetic catalysts. In this synthesis route, a mixed factorial experimental design reported in Table 3.2 was applied to explore the next synthesis conditions: CF-W/Fe₃O₄ ratio (1/1 - 2/1 w/w) and CF-W impregnation time (1 - 2 h) with Fe₃O₄.

Table 3.1 FAME formation (%) obtained from transesterification with magnetic cigarette filter-based catalysts prepared by different conditions of route 1

<i>Catalyst</i>	<i>Soaking time, min</i>	<i>Impregnation time, h</i>	<i>CBM/Fe₃O₄, w/w</i>	<i>Washing agent</i>	<i>FAME, %</i>
C1-R1	20	1.0	0.5/1.0	H ₂ O	33.70
C2-R1	20	1.5	1.0/1.0	NaOH	51.10
C3-R1	20	2.0	1.5/1.0	NW	17.36
C4-R1	40	1.0	1.0/1.0	NW	90.72
C5-R1	40	1.5	1.5/1.0	H ₂ O	27.48
C6-R1	40	2.0	0.5/1.0	NaOH	66.04
C7-R1	60	1.0	1.5/1.0	NaOH	85.53
C8-R1	60	1.5	0.5/1.0	NW	87.14
C9-R1	60	2.0	1.0/1.0	H ₂ O	58.32

NW: No washing

Note that the synthesis and loading of magnetite were carried out using the same quantity of reagents and the protocol described for Route 1. CF-W were ground into shorter fibers and added to a solution of sodium hydroxide, sodium citrate, and aluminum nitrate. In this case, no soaking time was used prior to the addition of the metal precursor; therefore, iron sulfate heptahydrate solution was added immediately. At the end of the reaction, the product was separated from the medium, and the same final cleaning and drying procedure was applied as that used for the catalysts obtained from Route 1.

The catalysts prepared from both synthesis routes were evaluated for the transesterification of commercial soybean oil (as a source of fatty acids) and methanol. The reaction conditions for testing the catalyst preparation routes were an oil/methanol molar ratio of 1/110 and 15 wt% of the catalyst with respect to oil at 60 °C for 5 h. After the reaction, the catalysts were easily separated from the medium using a magnet, resulting in the formation of three phases, namely unreacted alcohol, FAME, and glycerol. The alcohol was removed via evaporation in an oven operated at 100 °C for 12 h. The amount of FAME in the reaction product was quantified according to the European standard EN 14103.

The results of FAME formation obtained with the magnetic catalysts were utilized as the response variable to perform statistical analysis of the experimental design using MiniTab ® software. For Route 1, the signal-to-noise ratio (S/N) was calculated with FAME formation and applied in the

analysis of variance using the “bigger is better” approach because the objective was to maximize the catalytic performance of the tested materials. On the other hand, the statistical analysis of Route 2 was performed using the raw values of FAME formation. The results of both experimental designs allowed to identify the impact of the tested synthesis variables from each route on the catalytic properties of magnetic cigarette filter-based catalysts and the best conditions for their preparation.

Table 3.2 FAME formation (%) obtained from transesterification with magnetic cigarette filter-based catalysts prepared by different conditions of route 2

<i>Catalyst</i>	<i>CF-W/Fe₃O₄, w/w</i>	<i>Impregnation time, h</i>	<i>FAME, %</i>
C1-R2	1.0/1.0	1	78.09
C2-R2	1.0/1.0	2	95.96
C3-R2	1.5/1.0	1	63.12
C4-R2	1.5/1.0	2	94.17
C5-R2	2.0/1.0	1	83.35
C6-R2	2.0/1.0	2	93.20

3.2.3 Kinetic analysis of biodiesel transesterification using magnetic cigarette filter-based catalysts

A preliminary study was performed to define the best transesterification conditions using the best catalyst where the reaction temperature (50, 60, and 70 °C), oil/methanol molar ratio (1/10, 1/30, and 1/50), and the amount of catalyst with respect to oil (5, 15 and 25 wt%) were analyzed. The best oil/methanol molar ratio and catalyst percentage were applied to quantify transesterification kinetics at 50, 60, and 70 °C. The transesterification rate constants for biodiesel production using magnetic cigarette filter-based catalysts were estimated from the experimental kinetic data and models reported by Rezayan and Taghizadeh (2018) and Ashok et al. (2021), while the transesterification activation energy (E_a , kJ/mol) was calculated using linear regression of the Arrhenius equation (Bibeau et al., 2024). The tested kinetic models are described in expressions corresponding to the pseudo-first- (E1) and pseudo-second- (E2) order models (Rezayan and Taghizadeh, 2018; Ashok et al., 2021).

$$-\ln(1 - X_{ME}) = k_1 t \quad (E1)$$

$$\frac{X_{ME}}{1 - X_{ME}} = k' C_{Me0} C_{OH0} t \quad (E2)$$

3.2.4 Catalyst reusability tests

A catalyst reusability study was conducted using the best sample and conditions applied in the transesterification kinetic analysis. The first transesterification was performed at 60 °C and, after which the catalyst was recovered from the medium using a magnet, washed with 30 mL ethanol at 25 °C for 30 min, and subsequently dried at 100 °C for 12 h. This procedure was performed twice. The catalyst was then reactivated in a tubular furnace at 400 °C for 1 h under N₂ flow. This material was reused for transesterification under the same reaction conditions utilized in the first catalytic cycle, and its performance was compared and analyzed.

3.2.5 Physicochemical characterization of precursors, catalysts and biodiesel

The materials involved in the preparation of the catalysts (i.e., cellulose acetate fibers from cigarette filters, CBM from CF-W pyrolysis, and magnetite), and the best catalyst from each synthesis route were characterized by X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to determine their crystalline phases and functional groups. Elemental analysis of selected samples was performed using Energy Dispersive X-ray Spectrometry (EDS), and their morphologies were observed using Scanning Electron Microscopy (SEM). N₂ adsorption isotherms were quantified and used to determine textural properties of catalyst samples. The characterization conditions and equipment used in these analyses are reported in Supporting Information. On the other hand, some important parameters for evaluating biodiesel quality were also determined. Biodiesel viscosity and density were determined according to NMX-C-240-ONNCCE-2013, while its water amount (%) and acid value were determined according to ASTM D2709 and D664, respectively.

3.3 Results and discussion

3.3.1 Performance of magnetic cigarette filter-based catalysts in biodiesel transesterification

The transesterification results for the catalysts obtained via Route 1 are listed in Table 3.1. Initially, the activity of CBM without Fe₃O₄ impregnation was evaluated in soybean oil transesterification using the same reaction conditions applied to test the catalysts synthesized from both routes. FAME formation of CBM was < 1% indicating that this material did not exhibit catalytic properties. Therefore, the addition of magnetite conferred both magnetic and catalytic properties to the CBM.

FAME formation between 17 and 91% was obtained from magnetic catalysts prepared via Route 1, see Table 3.1. Overall, the transesterification properties of the magnetic catalysts prepared via Route 1 increased with NaOH soaking time and decreased with time for magnetite impregnation, see Figure 3.2. The best experimental conditions to achieve the highest FAME formation for the Route 1 catalysts were identified using S/N ratio analysis, see Figure 3.2 and Table 3.3. These conditions were as follows: CBM/NaOH soaking time of 60 min, impregnation time of 1 h, CBM/magnetite weight ratio of 1/1, and previous treatment of CBM with NaOH. It is important to highlight that the previous treatment of CBM via NaOH soaking improved the surface hydrophilicity, and consequently, a longer soaking time (60 min) allowed for better incorporation of the hydrophilic group (-OH), which can favor the aggregation of magnetite particles and their precipitation on the CBM surface (Picasso et al., 2012; Islam et al., 2017; Park et al., 2023).

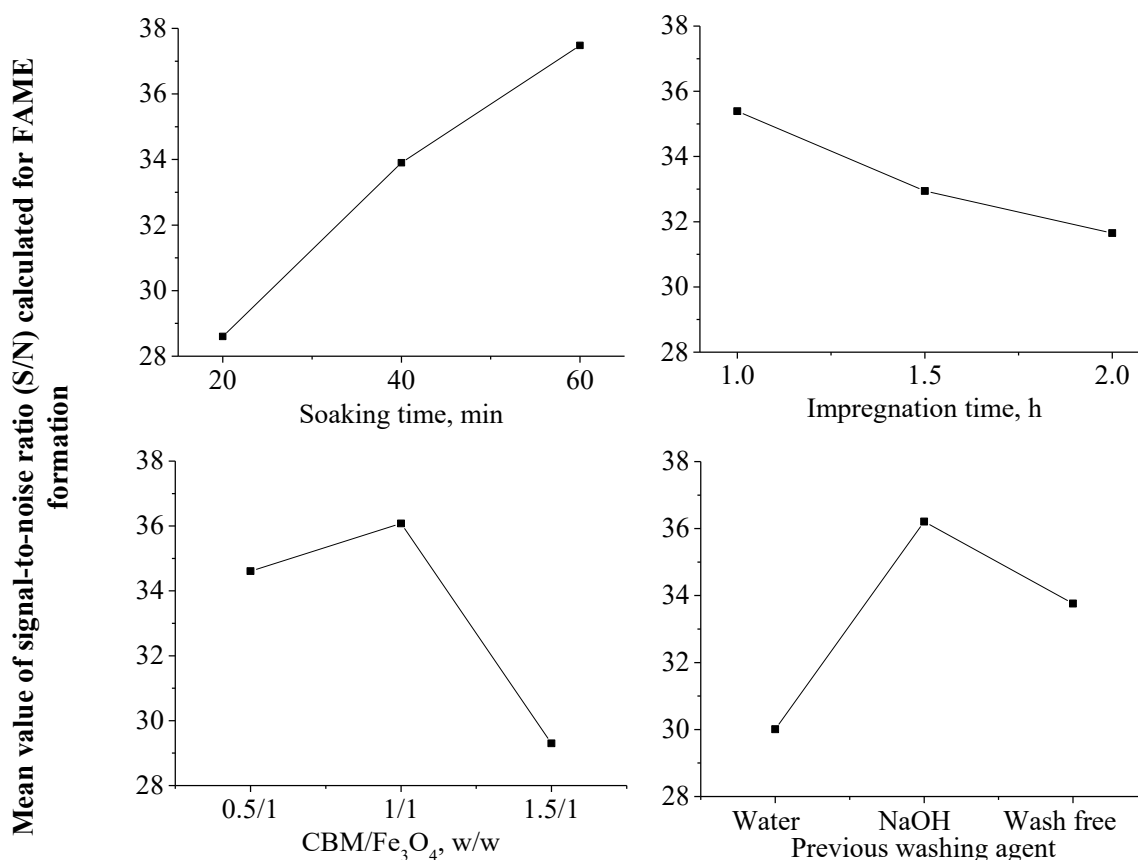


Figure 3.2 S/N ratio analysis of the preparation conditions tested to obtain magnetic cigarette filter-based catalysts using Route 1

On the other hand, an impregnation time of 1 h helped to obtain higher FAME formation in comparison with samples prepared with impregnation times of 1.5 and 2 h. Note that the synthesis of magnetite particles is a fast process, and exceeding this time can promote the formation of undesired compounds due to magnetite oxidation, as noted by Gnanaprakash et al. (2007) and Martínez-Mera et al. (2007). ANOVA results showed that the influence of tested variables from Route 1 on catalyst properties followed the trend: soaking time > carbon/magnetite ratio > NaOH treatment > impregnation time.

Table 3.3 Anova of tested catalyst preparation conditions using route 1

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>Impact level</i>
Soaking time, min	120.02	60.01	1
Impregnation time, h	21.62	10.81	4
Carbon-based material/Fe ₃ O ₄ , w/w	76.33	38.16	2
Previous washing agent	58.38	29.19	3
Total	276.37		

Catalysts prepared with cellulose acetate fibers derived from cigarette filters (Route 2) showed higher FAME formation percentages than those obtained with carbon-based catalysts (Route 1), see Table 3.2. Some catalyst samples prepared via Route 2 exhibited up to 96% FAME formation. It is important to note that the material used as the catalyst support did not require NaOH soaking prior to the addition of the metal precursor, in contrast to CBM, because this material is composed of cellulose acetate fibers, which are characterized by being hydrophilic and porous, facilitating magnetite particle loading (Vatanpour et al., 2022; Wang et al., 2022). Overall, it was observed that an increase in impregnation time favored the catalytic properties of the magnetic materials generated by Route 2. The results showed that the highest FAME percentages were obtained with 2 h of impregnation time, which corresponded to the catalyst samples from experiments 2, 4, and 6 of Table 3.2.

ANOVA of this experimental design confirmed that the tested variables had a statistically significant effect on the catalyst properties, that is, $p\text{-value} = 0.047$ for the impregnation time and $p\text{-value} = 3.9 \times 10^{-4}$ for the cigarette filters/Fe₃O₄ ratio, (see Table 3.4).

Catalyst 2 from Route 2 (i.e., sample C2-R2) was selected to optimize the reaction conditions and continue the kinetic analysis of transesterification to obtain biodiesel. This magnetic material was obtained using a weight ratio of cigarette filters/Fe₃O₄ of 1/1 and an impregnation time of 2 h. It is worth mentioning that the catalysts obtained from Route 1 were not considered for further reaction experiments because their performance was lower than that of catalysts prepared with cellulose

acetate. Route 2 was simpler because the precursor did not require pyrolysis or an additional step to reduce material hydrophobicity with NaOH to favor magnetite loading (Park et al., 2023). Therefore, the synthesis conditions of Route 2 offer more advantages than those of Route 1 for preparing magnetic catalysts with better properties for obtaining biodiesel.

Table 3.4 Anova of tested catalyst preparation conditions using route 2

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>p-value</i>
Cigarette filters/Fe ₃ O ₄ , w/w	261.38	130.69	0.047
Impregnation time, h	1250.11	1250.11	3.9x10 ⁻⁴
Interaction Cigarette filters/Fe ₃ O ₄ , w/w - Impregnation time, h	218.05	109.02	0.066
Error	148.84	24.81	
Total	1878.37		

Finally, it should be noted that all the prepared catalysts from both the synthesis routes were easily recovered from the reaction medium using a magnet, as shown in Figure 3.3. The magnetic properties of these catalysts help to avoid the use of additional equipment and reduce energy consumption for their separation, generating potential benefits in terms of biodiesel cost and environmental impact (Thangaraj et al., 2019; Wilkanowicz et al., 2020).

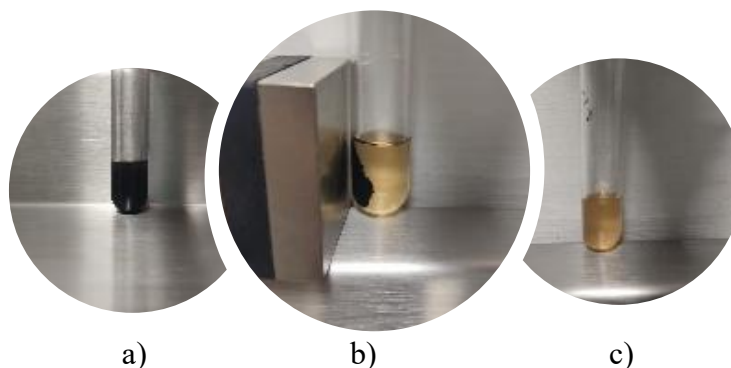


Figure 3.3 Separation of the magnetic catalyst using a magnet. Illustrations: a) mixture obtained at the end of the reaction where the catalyst is dispersed in the medium, b) catalyst separation with the help of a magnet, and c) products from transesterification once the catalyst has been separated.

3.3.2 Transesterification kinetic analysis to obtain biodiesel using the best magnetic cellulose acetate catalyst

Table 3.5 shows the results of the sensitivity analysis performed under different transesterification conditions to obtain biodiesel with catalyst 2 from Route 2. The highest percentages of FAME formation were obtained for experimental conditions 8 and 9, where a higher soybean oil/methanol molar ratio and/or an increase in the transesterification temperature was required to enhance biodiesel production. Transesterification is characterized by its reversibility, and consequently, the reaction is favored towards the products with the alcohol amount. On the other hand, an increase in temperature improves the mixing of alcohol and oil by decreasing the system viscosity, which enhances mass transfer (Kamel et al., 2018; Singh et al., 2019). The best reaction conditions obtained from the statistical analysis were a soybean oil/methanol molar ratio of 1/50, 70 °C, and 5 wt% of catalyst with respect to the oil.

Table 3.5 FAME formation (%) obtained with the catalyst C2-R2 under different transesterification conditions

<i>Conditions for transesterification to obtain biodiesel</i>				
<i>Experimental condition</i>	<i>Soybean oil/methanol molar ratio</i>	<i>Temperature, °C</i>	<i>Catalyst respect to oil, wt%</i>	<i>FAME, %</i>
1	1/10	50	5	25.20
2	1/10	60	15	26.98
3	1/10	70	25	54.14
4	1/30	50	15	42.29
5	1/30	60	25	37.84
6	1/30	70	5	82.03
7	1/50	50	25	60.04
8	1/50	60	5	89.20
9	1/50	70	15	98.68

Transesterification kinetics were carried out to assess the impact of both reaction temperature and time on biodiesel production, and the results are shown in Figure 3.4.

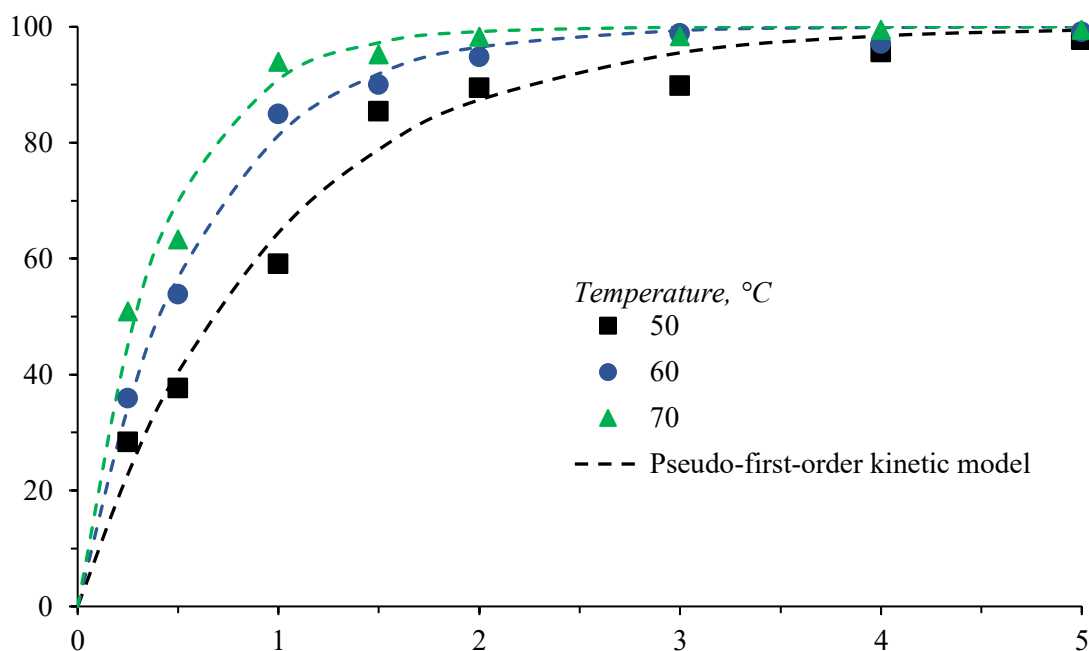


Figure 3.4 Transesterification kinetics of soybean oil with methanol using the best magnetic cigarette filter-based catalyst

The formation (%) of methyl esters improved with increasing transesterification temperature and time, in agreement with previous studies (Verma and Sharma, 2016; Singh et al., 2019). The transesterification system used to obtain biodiesel is endothermic; therefore, the reaction temperature is a crucial factor that directly affects the amount of biodiesel produced (Suzihaque et al., 2022). After 90 min of reaction, FAME formation was higher than 85% at all tested temperatures using the best magnetic cellulose acetate catalyst, reaching equilibrium after 5 h. The results also indicated that the highest FAME formation was 99.5% at 70 °C after 4 h of reaction.

The transesterification kinetics obtained at different temperatures were fitted to the pseudo-first-order and pseudo-second-order models, and the calculated transesterification rate constants and determination coefficients (R^2) are presented in Table 3.6. The pseudo-first-order equation ($R^2 = 0.98$ - 0.99) was the most adequate model to describe the experimental data and offered a better performance than that of the pseudo-second-order equation ($R^2 = 0.91$ - 0.95).

The literature indicates that the pseudo-first-order model assumes that the activities of triglycerides, diglycerides, and monoglycerides are the same in the reactive system and that alcohol is in excess (Alenezi et al., 2016; Farid et al., 2024). The activation energy (E_a) calculated for the transesterification of soybean oil using the best magnetic cellulose acetate catalyst was 39 kJ/mol, indicating that this reactive system was heterogeneous and chemically controlled (Jain et al., 2011). Kaur and Ali (2014) have indicated that E_a from 26 to 84 kJ/mol is characteristic of heterogeneous

transesterification, moreover $E_a > 25$ kJ/mol has been associated with a chemically controlled transesterification (Kaur and Ali, 2015).

Table 3.6 Calculated rate constants using different kinetic models for the transesterification of soybean oil with methanol using the best magnetic cigarette filter-based catalyst

Temperature, °C	Kinetic model			
	Pseudo-first-order		Pseudo-second-order	
	k_1, min^{-1}	R^2	$k_2, \text{L mol}^{-1} \text{min}^{-1}$	R^2
50	0.0172	0.98	0.0264	0.93
60	0.0279	0.99	0.0373	0.91
70	0.0399	0.99	0.0691	0.95

Table 3.7 summarizes the FAME formation of different magnetic catalysts reported in various studies, which have been cited for comparison. These catalysts were prepared using iron salts derived from banana peel (Liu et al., 2015), *Jatropha* hulls (Zhang et al., 2017), cotton (Ghasemzadeh et al., 2022), and diaper waste (Chen et al., 2023). The results obtained with the magnetic cigarette filter-based catalysts are comparable to those reported for other catalysts under similar reaction conditions.

The results from the reusability catalyst studies indicated that the catalytic activity of the tested material decreased drastically after the first reaction cycle, where FAME formation of 24% was obtained with the catalyst used in a second reaction under the same operating conditions. This decrease in FAME formation can be attributed to catalyst deactivation, a common phenomenon in heterogeneous transesterification.

Catalyst deactivation can occur because of the deposition of impurities on the material surface. Previous studies have indicated that there is an accumulation of impurities (e.g., traces of glycerin, biodiesel, or unreacted triglycerides) on the catalyst surface during the first reaction cycle that cannot be removed by washing (Ambat et al., 2019). However, it should be noted that the catalytic activity of magnetic materials after their first use can vary considerably (Gardy et al., 2018). The catalyst deactivation in magnetic catalysts has been mainly attributed to the susceptibility of magnetite to oxidation (Alemán-Ramírez et al., 2023).

Figure 3.5 illustrates the proposed transesterification mechanism to obtain biodiesel using a magnetic cigarette filter-based catalyst. It should be noted that the magnetite particles added to the supports during the synthesis routes exhibited not only magnetic but also catalytic properties because of the Lewis acidic character of the Fe 3d orbitals.

Table 3.7 Literature survey of magnetic catalysts used in biodiesel production by transesterification

<i>Catalyst</i>	<i>Transesterification conditions</i>	<i>FAME, %</i>	<i>Reference</i>
Ca/Al/Fe ₃ O ₄	C: 6 wt%, t: 3 h, T: 65 °C, MR: 1/15 (RO/M)	93.53	Tang et al. (2012)
Magnetic carbonaceous solid acid from banana peel	C: 3 wt%, t: 8 h, T: 80 °C, MR: 1/33 (OA/M)	94	Liu et al. (2015)
Sulfamic acid functionalized silica-coated crystalline Fe/Fe ₃ O ₄ core/shell magnetic nanoparticles	t: 4 h T: 70 °C OA	100	Wang et al. (2015)
Magnetic cellulose microsphere supported on H ₃ PW ₁₂ O ₄₀	C: 15 wt%, t: 1.3 h, T: 60 °C, MR: 1/10 (TBO/M)	93.1	Han et al. (2016)
Magnetic carbonaceous acids from <i>Jatropha</i> hulls	C: 7.5 wt%, t: 7.5 h, T: 180 °C, MR: 1/18 (JO/M)	95.9	Zhang et al. (2017)
Bamboo charcoal-based magnetic solid base catalyst	C: 2.5 wt%, t: 1 h, T: 60 °C, MR: 1/8 (SO/M)	98	Liu et al. (2018)
Potassium impregnated Fe ₃ O ₄ -CeO ₂ nanocatalyst	C: 4.5 wt%, t: 2 h, T: 65 °C, MR 1/7 (RO/M)	96.13	Ambat et al. (2019)
Sulfonated and magnetic catalyst from palm kernel shell	C: 3.66 wt%, t: 1.7 h, T: 65 °C, MR: 1/13 (WCO/M)	90.2	Quah et al. (2020)
MnFe ₂ O ₄ /graphene oxide	C: 3 wt%, t: 4 h, T: 65 °C, MR: 1/18 (WCO/M)	96.47	Bai et al. (2021)
Cotton/Fe ₃ O ₄ @SiO ₂ @H ₃ PW ₁₂ O ₄₀	C: 3 wt%, t: 3.5 h, T: 70 °C, MR: 1/21 (SO/methanol)	95.3	Ghasemzadeh et al. (2022)
Waste diaper-derived heterogeneous magnetic catalyst	C: 4 wt%, t: 4 h, T: 65 °C, MR: 1/9 (WCO/M)	96.4	Chen et al. (2023)
Magnetic carbon-based catalyst from solid waste (reed straw and electric furnace dust)	C: 7.75 wt%, t: 4.16 h, T: 74.15 °C, MR: 1/14.06 (SO/M)	99.89	Wang et al. (2024)
Carbon-based magnetic catalyst	C: 15 wt%, t: 5 h, T: 60 °C, MR: 1/110 (SO/M)	90.72	This study
Magnetic catalyst from cellulose acetate (cigarette filters waste)	C: 5 wt%, t: 5 h, T: 70 °C, MR: 1/50 (SO/M)	99.5	This study

C: catalyst load; t: reaction time; T: reaction temperature; MR: molar ratio; RO: rapeseed oil; M: methanol; OA: oleic acid; TBO: highly-acidic tree born oil; JO: *Jatropha* oil; SO: soybean oil; WCO: waste cooking oil; SO: sunflower oil

These acid sites polarize the OH bond of methanol to accept protons and contribute to the generation of alkoxide species (Faruque et al., 2020). Therefore, the alcohol used in the reaction is absorbed by the Lewis acid (Fe^{3+}) to form a Brønsted acid via nucleophilic substitution of the acid sites with the alcohol. The carbon of the carbonyl group of triglyceride forms an intermediate that dissociates into the alkyl ester and anion of diglyceride. The diglyceride anion then causes catalyst deprotonation, allowing regeneration to continue the catalytic cycle, see Figure 3.5. This process is subsequently repeated with the diglycerides and monoglycerides generated during the reaction, as described by Dos Santos-Durmdell et al. (2018) and Krishnan et al. (2021). Once transesterification is completed by obtaining alkyl esters, the catalyst can be reused in subsequent reactions (Lakshmi et al., 2020).

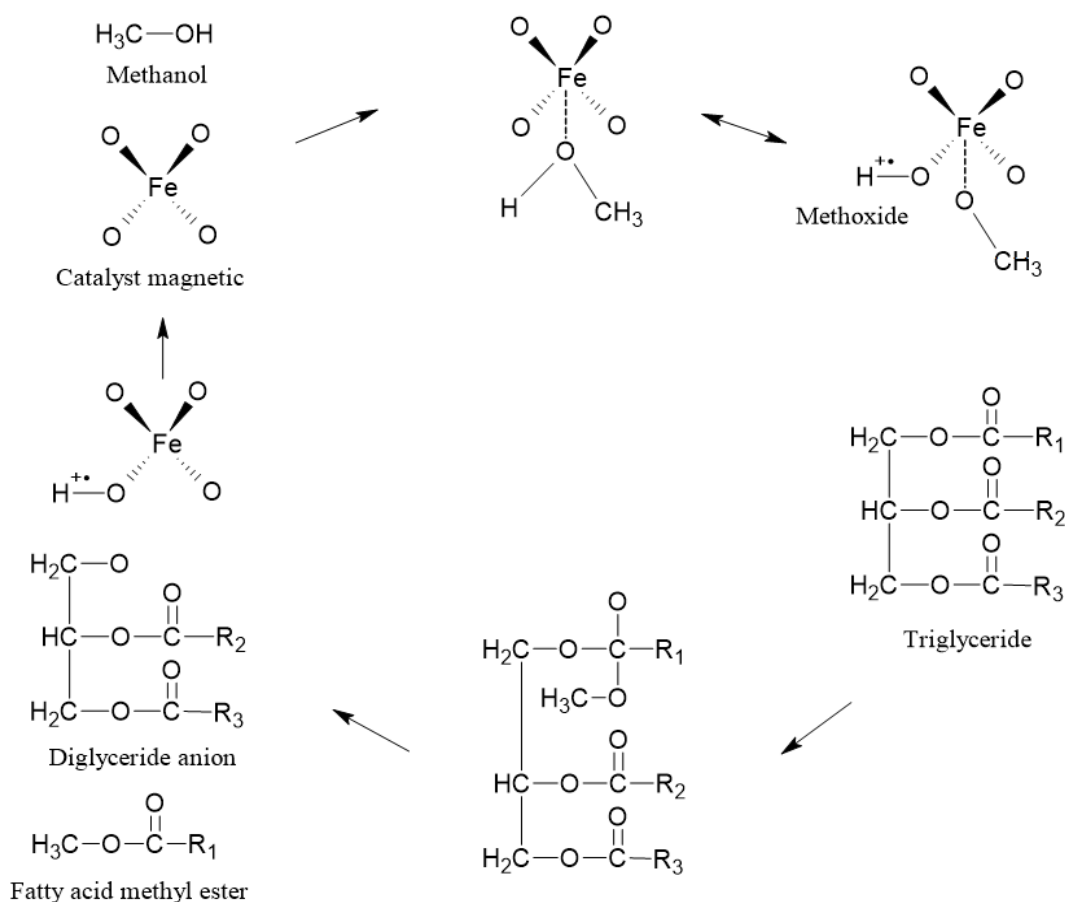


Figure 3.5 Proposed mechanism for the transesterification of triglycerides with methanol using the best magnetic cigarette filter-based catalyst.

3.3.3 Physicochemical characterization of precursors, catalysts and biodiesel

The crystalline structures of each material involved in catalyst preparation were determined using X-ray diffractograms (Figure 3.6). The diffractograms reported in Figure 3.6(a) correspond to the

unwashed cigarette filters (CF-UW), washed cigarette filters (CF-W), and carbon-based materials (CBM) obtained from the pyrolysis of CF-W at 400 °C.

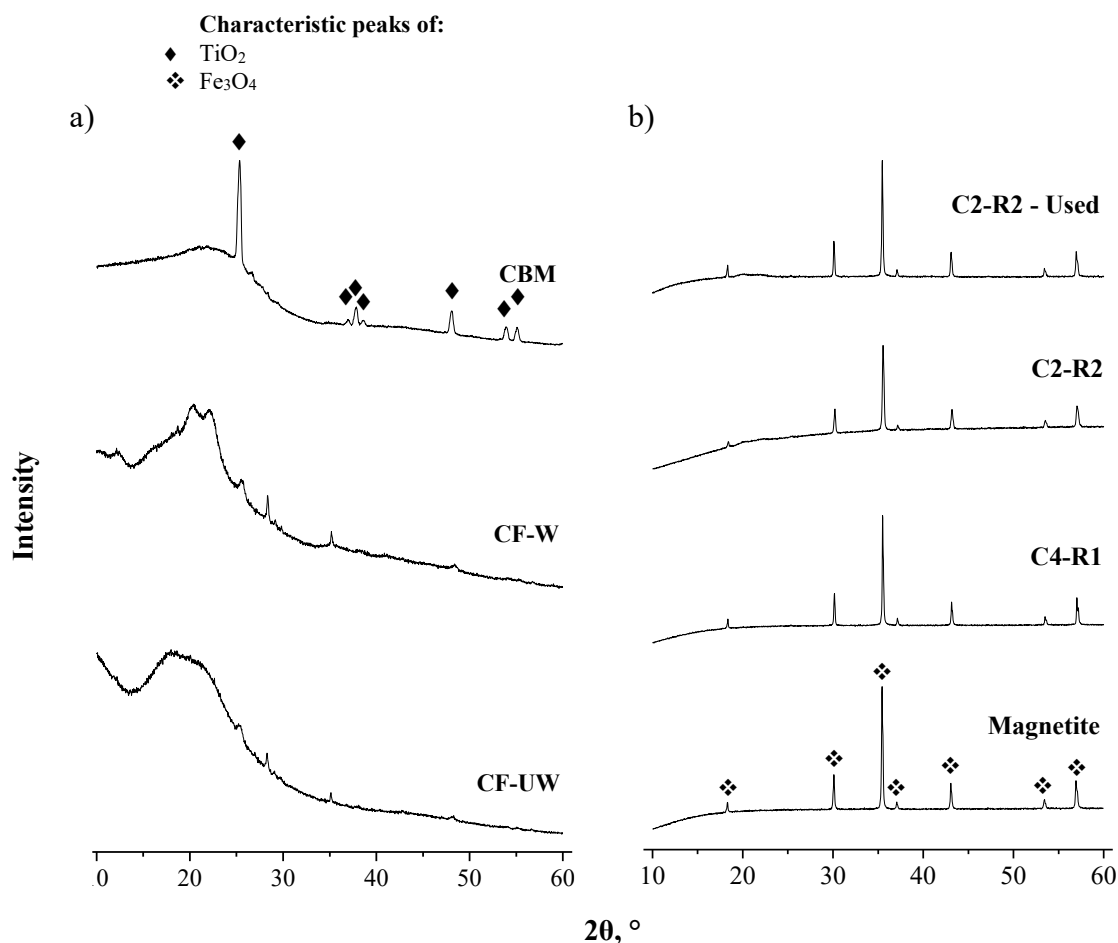


Figure 3.6 X-ray diffractograms of a) precursors used in the catalyst preparation; b) magnetite and the best magnetic catalysts from route 1 (C4-R1) and route 2 (C2-R2 before and after use).

The three diffractograms contain a peak at 20 °2θ associated with the disordered region of cellulose acetate present in washed and unwashed samples of cigarette filters where an amorphous region is identified because of the acetyl groups of this polymer (Imam et al., 2020). However, the peak located at 20 2θ ° in CBM sample corresponded to a graphitic structure (Ogundare et al., 2017). The remaining peaks identified in the CBM diffractogram that are located at 25.3, 37, 37.9, 38.7, 48, 54, and 55.1 °2θ belong to titanium dioxide, an additive used in the cigarette filter production, whose purpose is to induce the photodegradation of cellulose acetate (Lee et al., 2014; Lyu et al., 2021; Lee and Kwak, 2022).

On the other hand, the diffractograms displayed in Figure 3.6(b) correspond to magnetite, the carbon-based material/magnetite catalyst (C4-R1), and the cellulose acetate-based/magnetite catalyst (C2-R2) derived from washed cigarette filters before and after (C2-R2-used) being used in transesterification. All diffractograms showed the same peaks localized at 18.3, 30.2, 35.3, 43.2, 53.5, and 57.3 °2 θ , which were associated with the reverse spinel cubic crystal structure of magnetite (Ren et al., 2017; Alqadami et al., 2018). These samples displayed higher crystallinity than the raw precursors due to the presence of this magnetic compound. Therefore, the diffraction peaks belonging to the amorphous structures of the acetate and graphitic structures of the carbon-based support were not observed.

Figure 3.7(a) shows the FTIR spectra corresponding to washed and unwashed samples of cigarette filters, as well as the carbon-based material. Several characteristic absorption bands of cellulose acetate were identified in the spectrum of cigarette filters.

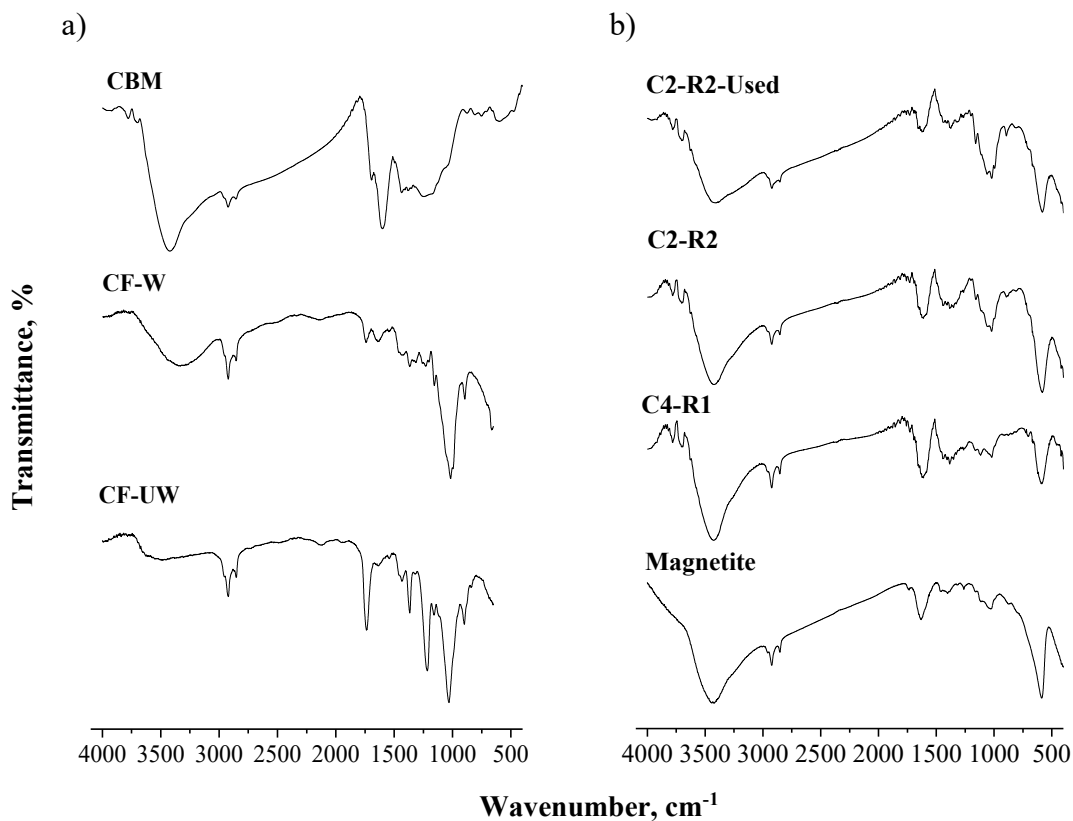


Figure 3.7 FTIR spectra of a) precursor and magnetite; b) magnetite and the best magnetic catalysts from route 1 (C4-R1) and route 2 (C2-R2 before and after use).

The main absorption bands are located at 1731, 1213 and 1029 cm⁻¹, and they were associated with carbonyl group (C = O) (Aboamera et al., 2019; Mahto et al., 2022), acetyl ester group (CH₃ – C = O) (Khan et al., 2023), and ether group (C – O – C) (Khoshnevisan et al., 2019; Khan et al.,

2023b), respectively. The three spectra reported in Figure 3.7(a) contain an absorption band located at $\sim 3400\text{ cm}^{-1}$ belonging to OH group (Jain et al., 2019; El-Dib et al., 2020); however, the band observed in CF-W spectrum was more pronounced, possibly because of the washing process that was applied to the filters (Zuluaga-Parra et al., 2020).

In the CBM spectrum, the absorption bands located at $2900\text{--}2850\text{ cm}^{-1}$ correspond to CH stretching of methyl groups (Fraga et al., 2020; Ghelich et al., 2020; Kokilavani et al., 2020), the absorption band located at $\sim 1700\text{ cm}^{-1}$ was attributed to the C=O group of carboxylic acids (Salehian et al., 2013; Jatoi et al., 2020), while the absorption band located at 1600 cm^{-1} belongs to C=C bonds (Vega et al., 2010; Asemani and Rabbani, 2020). The small absorption band at 1400 cm^{-1} and broad absorption band at $\sim 1200\text{ cm}^{-1}$ were associated with C-H₂ and CO stretching, respectively, with the latter corresponding to ether, ester, and carboxylic acid groups (Han et al., 2016; Özdemir et al., 2016; Jatoi et al., 2020).

FTIR spectrum of magnetite also contains the first four absorption bands described above (3400 , 2900 , 1700 , and 1600 cm^{-1}). In addition, two more absorption bands are observed at 1024 and 584 cm^{-1} , the first one (1024 cm^{-1}) was attributed to the stretching vibrations of SO_4^{2-} that did not react during the magnetite synthesis (Ren et al., 2017; Shahid and Choi, 2020); and the second absorption band corresponds to Fe-O stretching vibrations (Jain et al., 2019; Singh et al., 2020; Zheng et al., 2020), which confirmed that magnetite was obtained. These bands were also observed in the FTIR spectra of catalysts, see Figure 3.7(b). However, some absorption bands were more pronounced, such as the band belonging to the sulfate group in the C2-R2 catalyst because the structure of cellulose acetate fibers allowed a higher entrapment of the components during impregnation (Chen et al., 2020). The characteristic absorption band of magnetite (584 cm^{-1}) was observed, verifying the presence of this magnetic compound in the synthesized catalysts, which was more evident for the C2-R2 catalyst sample.

The elemental compositions of the precursors and selected catalyst samples obtained using each preparation route are listed in Table 3.8. It was observed that the CF-UW and CF-W samples showed high C content ($\sim 50\%$) due to their structural nature (Hudaib et al., 2024), and this content increased with the carbonization process up to 69% for CBM sample. However, the catalysts prepared by Route 1 had a lower C content, but double O content, with respect to the support, due to the presence of magnetite. This result was also observed for the catalysts prepared using cellulose acetate as support; however, the C content was even lower. Approximately a quarter of the catalysts were composed of Fe (i.e., $20\text{--}28\%$). A correlation between the Fe content and the catalyst properties was found. Catalyst 4 from Route 1 (C4-R1) and catalyst 2 from Route 2 (C2-R2) showed the highest percentages of

FAME formation and Fe content (28.6 and 28.2%, respectively). The composition of pure magnetite agrees with the theoretical composition of Fe (72.36%) and O (27.64%) according to its structure (Shrivastava et al., 2023).

Table 3.8 Elemental analysis of the precursors and samples of magnetic cigarette filter-based catalysts

<i>Sample</i>	<i>Element, %</i>							
	<i>C</i>	<i>H</i>	<i>N</i>	<i>O</i>	<i>Fe</i>	<i>Na</i>	<i>Si</i>	<i>Others</i>
CF-UW	46.7	5.65	0	47.65	-	-	-	-
CF-W	42.8	6.06	0	51.14	-	-	-	-
CBM	69.1	4.00	0	24.14	0.14	0.2	0.49	1.93
Magnetite	-	-	-	28.07	70.61	0.3	0.73	0.29
C3-R1 (worst performance)	33.7	2.46	0	38.28	19.82	3.36	1.23	1.15
C4-R1 (best performance)	14.3	2.36	0	47.35	28.57	6.38	0.49	0.55
C9-R1 (intermediate performance)	28.9	2.15	0	38.70	21.17	6.95	0.99	1.13
C2-R2 (best performance)	13.5	2.11	0	47.21	28.23	7.73	0.76	0.47
C3-R2 (worst performance)	16.9	2.6	0	48.48	25.01	5.69	0.53	0.79
C5-R2 (intermediate performance)	20.0	3.38	0	47.19	23.06	4.64	0.96	0.78

CF-UW: unwashed cigarette filters, CF-W: washed cigarette filters, CBM: carbon-based material, R1: route 1, R2: route 2.

EDX analysis confirmed the presence of other elements such as Si, Ti, Na, S, Al, and Mn with compositions ranging from 1.32 to 9.07 %, depending on the material and its source. S, Al, and Na contents can be explained by the preparation method, but the remaining elements can be found in the raw material. Ti can be present in the form of oxides because of the additives used in the manufacturing of cigarette filters (Das and Gebru, 2017), confirming its presence via the X-ray diffractogram shown in Figure 3.6(a).

Figure 3.8 shows the morphology of selected support and catalyst samples. Smooth disordered fibers were observed (Tehrim et al., 2020; Zhang et al., 2020) with a Y-shaped appearance, which was associated with cellulose acetate from unwashed and washed cigarette filter waste. These results agree with those reported by Soltani et al. (2014). Note that the fibers from the unwashed cigarette filters contained particles adhered to the surface because of the impurities present, which were possibly trapped during cigarette consumption. In contrast, the fibers from the washed cigarette filters showed a cleaner surface with scarce and smaller particles.

The morphology of CBM reported in Figure 3.8(c) has the same structure as the non-carbonized fibers, but with a smaller size and without porosity (Xiong et al., 2019). C4-R1 catalyst was amorphous and had small polyhedral particles agglomerated over the entire surface, corresponding to magnetite (Torres-Gómez et al., 2019). In the SEM images of the C3-R1 and C9-R1 samples (i.e., catalysts with the worst and intermediate performances), a large part of the support surface was not loaded with magnetite, which could explain their low catalytic performance.

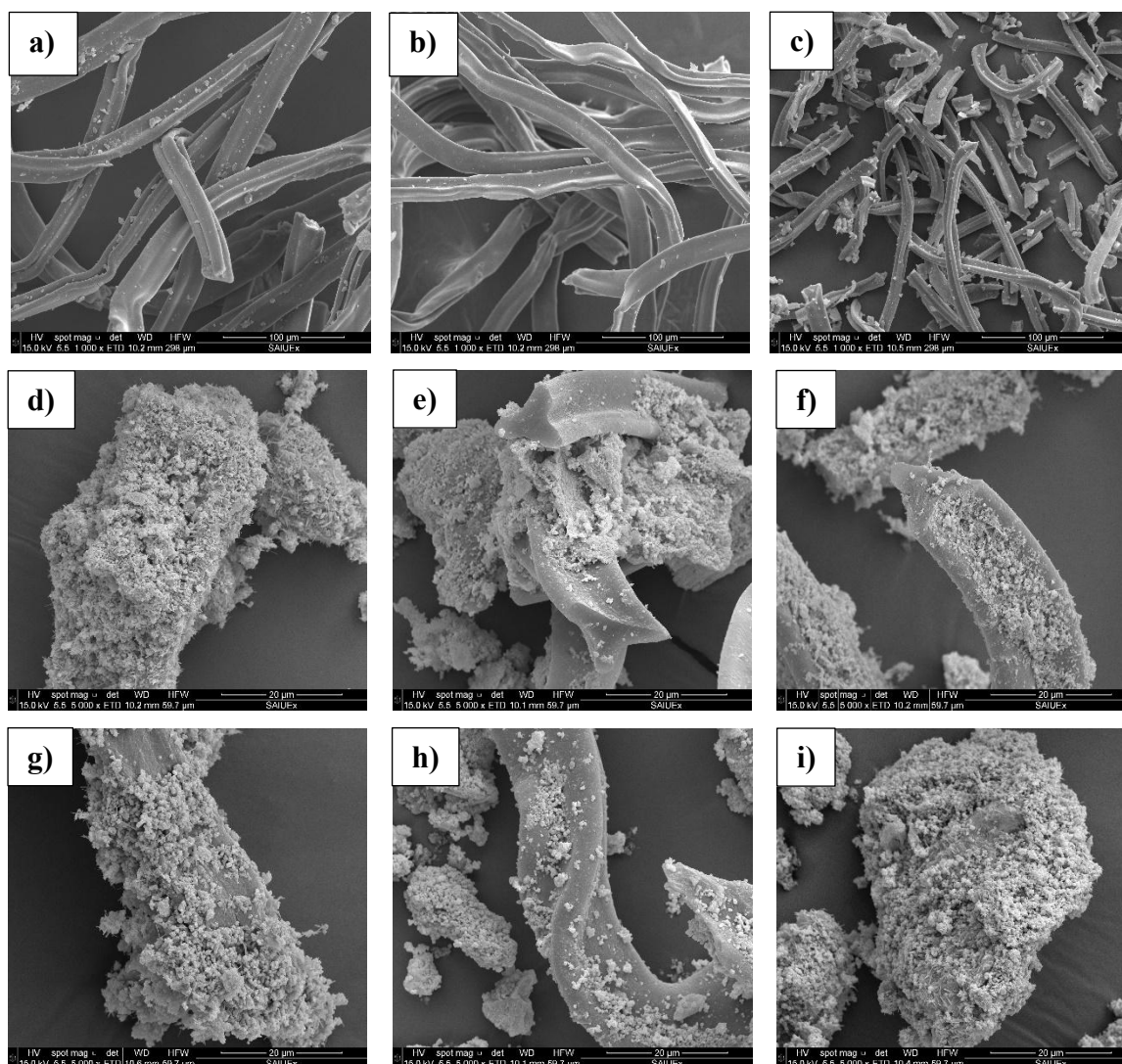


Figure 3.8 SEM image of precursors and samples of magnetic cigarette filter-based catalysts. Samples: a) cellulose acetate from unwashed cigarette filter wastes, b) cellulose acetate from washed cigarette filter wastes, c) carbon based-material, d) catalyst 4 of route 1 (best performance), e) catalyst 3 of route 1 (worst performance), f) catalyst 9 of route 1 (intermediate performance), g) catalyst 2 of route 2 (best performance), h) catalyst 3 of route 2 (worst performance), and i) catalyst 5 of route 2 (intermediate performance).

The surfaces of C2-R2 (best performance) and C5-R2 (intermediate performance) catalysts were very similar, and only a small section without adhered magnetite particles was observed. C3-R2 catalyst (worst performance) exhibited a larger area free of these particles. Phenomenon mentioned above was verified using secondary and backscattered electron images, see Figure 3.9. In these images, the C2-R2 catalyst shows a brighter surface, indicating the presence of Fe on most of its surface, compared to the surface of C3-R2 catalyst, which is less bright. Similarly, it was found that O was distributed across almost the entire surface, with a higher concentration in areas where Fe was identified. In addition to the polyhedral magnetite particles, a few needle-shaped particles were observed in the catalyst samples, see Figure 3.8(d)-(i), either in aggregates or alone, which could correspond to goethite (α -FeOOH) (He and Traina, 2007; Strauss et al., 2013). This compound acts as a template or an intermediate for magnetite formation (Di Iorio et al., 2019). It is important to note that the characteristics diffraction peaks (25, 39, 43, 48, 63, 70 and 72 $^{\circ}2\theta$) and the FTIR absorption bands at 895 and 796 cm^{-1} (Fe – O – OH) of goethite (Kong and Wilson, 2017; Liu et al., 2019) were not identified in the characterization results of these materials. This was due to the low number of needle-shaped particles observed in the micrographs.

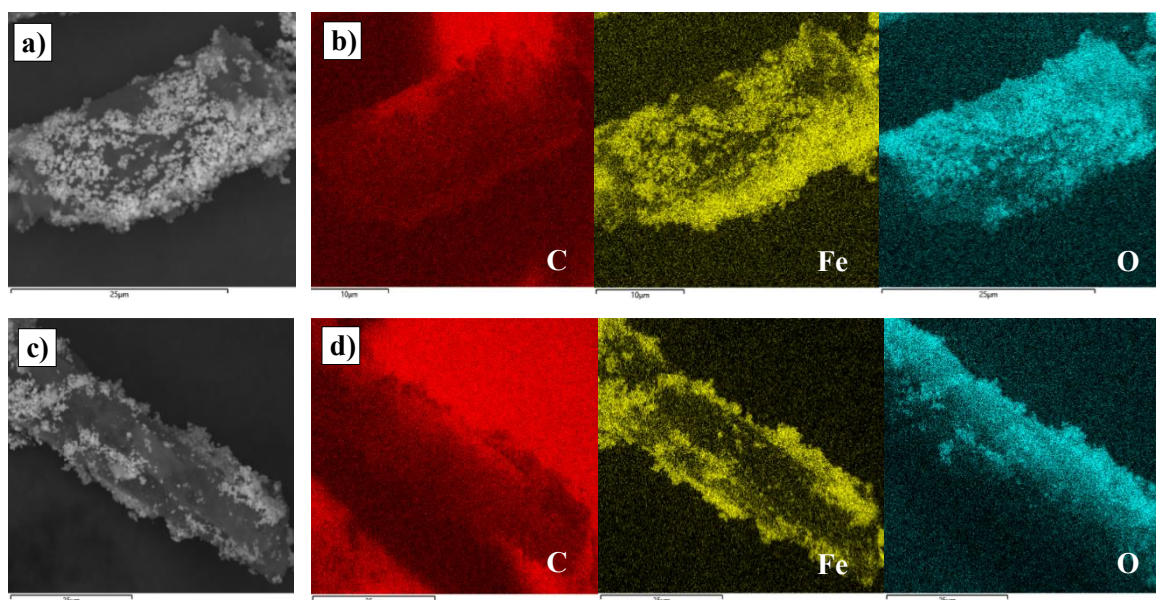


Figure 3.9 Secondary electron (SE) and backscattered electron (BSE) images of a,b) catalyst 2 of route 2 (best performance) and c,d) catalyst 3 of route 2 (worst performance).

The textural parameters of the selected catalysts are listed in Table 3.9. The magnetic cigarette filter-based catalysts exhibited low specific surface areas of 16 and 22 m^2/g , while the carbon-based support had a surface area of 35 m^2/g . The decrease in the specific surface area after the impregnation of the carbon-based supports was likely due to the pore blockage caused by the deposition of

magnetite particles (Duan et al., 2020; El-Sayed et al., 2021). The micropore volume was 0.003-0.007 cm³/g, while the mesopore volume was slightly higher 0.038-0.091 cm³/g. It is possible that the low values of the surface area and volume of micro- and mesopores were due to the method chosen to obtain the carbon-based material besides the impregnated materials did not undergo activation (Yang et al., 2010; Zhang et al., 2019). The catalysts prepared directly from cigarette filter wastes (Route 2) showed higher surface areas (i.e., 16 - 90 cm²/g), as well as a slightly larger micro and mesopore volumes than those of the catalysts from Route 1. This result was associated with the nature of feedstock used in catalyst preparation, as cellulose acetate is characterized by a high specific surface area and high porosity (Angel et al., 2020).

Table 3.9 Textural parameters of CBM and samples of magnetic cigarette filter-based catalysts

<i>Material</i>	<i>S_{BET}, m²/g</i>	<i>V_{micropores}, cm³/g</i>	<i>V_{mesopores}, cm³/g</i>
CBM	35.14	0.007	0.047
C3-R1 (worst performance)	21.61	0.007	0.091
C4-R1 (best performance)	16.07	0.003	0.038
C9-R1 (intermediate performance)	16.46	0.004	0.066
C2-R2 (best performance)	89.75	0.010	0.099
C3-R2 (worst performance)	74.80	0.009	0.091
C5-R2 (intermediate performance)	15.51	0.004	0.052

Table 3.10 shows the values of tested properties of biodiesel obtained from soybean oil using C2-R2 catalyst. These results were compared with the standards established in ASTM D6751. It was observed that all the properties are within the allowed ranges, which is essential to guarantee the biodiesel quality and its optimal performance in engines (Gülüm and Bilgin, 2021). In particular, it is crucial to control its viscosity, since a high value could affect the biofuel atomization, leading to inefficient combustion (Zhu et al., 2024).

Table 3.10 Characterization of biodiesel obtained from the transesterification of soybean oil and methanol using C2-R2 catalyst

<i>Property</i>	<i>ASTM 6751 range</i>	<i>Soybean oil biodiesel</i>
Specific density at 25 °C	0.86 – 0.90	0.886
Acid value, mg KOH/g	≤ 0.8	0.20
Water content, wt%	≤ 0.05	0.045
Viscosity at 40 °C, mm ² /s	1.9 – 6.0	5.56

3.4 Conclusions

Cellulose acetate obtained from cigarette filter waste and Fe_3O_4 were used for the preparation of new magnetic catalysts for biodiesel production via transesterification. Different catalyst samples were obtained from two preparation routes, and the best synthesis conditions were identified to tailor their catalytic properties. The results indicated that the synthesis route based on the direct application of cellulose acetate fibers from cigarette filters with magnetite loading was the best option for obtaining a magnetic catalyst that exhibited 99.5% FAME formation for the transesterification of soybean oil with methanol at 70 °C for 4 h. A direct correlation was observed between the iron composition of the synthesized catalysts and their transesterification properties. The loading of Fe_3O_4 particles on cellulose acetate-based materials obtained from cigarette filter waste provides both catalytic and magnetic properties. The transesterification system to obtain biodiesel using the best magnetic cigarette filter-based catalyst was endothermic and fitted with a pseudo-first-order kinetic model that was chemically controlled with an activation energy of 39 kJ/mol. However, the catalytic properties of this novel material were degraded after the first reaction cycle, indicating that more studies are required to optimize the synthesis conditions to extend its lifetime and to understand the source of catalyst deactivation. This study demonstrates the potential of magnetic catalysts prepared using a circular economy approach, as novel materials for resolving some of the current challenges and gaps related to biodiesel production and waste management.

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Chapter 4. Preparation and catalytic evaluation of magnetic materials derived from EDTA-functionalized cigarette filter waste for biodiesel production

Abstract

This chapter presents the development of magnetic catalysts from cigarette filter waste with and without EDTA functionalization through the hydrothermal carbonization method. The obtained materials were applied in the transesterification of soybean oil with methanol for biodiesel production. For this purpose, three series of catalysts were prepared: the first without functionalization, the second functionalized with 2 mmol of EDTA, and the third varying the EDTA concentration (1–3 mmol), with the aim of evaluating the influence of this chelating agent on the stability of the catalysts during their storage. The results showed that the catalysts functionalized with EDTA exhibited greater stability and catalytic activity, reaching FAME formation percentages higher than 90%, even after 90 days of storage. Therefore, the best EDTA-functionalized material was used to determine the optimal reaction conditions, which were 5 wt% catalyst relative to the oil weight, a soybean oil/methanol molar ratio of 1:15, and a temperature of 60 °C. In addition, the reusability of the best catalyst was evaluated, and it was determined that it can be used for 4 reaction cycles while maintaining percentages of FAME formation above 95%. Furthermore, the EDTA-functionalized catalysts that showed the worst, best, and intermediate performance were characterized by XRD and FTIR, confirming the presence of magnetite even at the end of the established storage period. This study highlighted the importance of using the chelating agent to prevent the oxidation of the magnetic compound (as in the case of non-functionalized materials), thereby preserving both magnetic and catalytic properties, and allowing for efficient recovery through magnetic separation.

4.1 Introduction

With the aim of reducing dependence on fossil fuels and simultaneously mitigating greenhouse gas emissions, which continue to significantly impact the planet, various renewable energy sources have been gradually developed and implemented in the transportation sector (Xuan, 2024). This is because the transportation sector is responsible for approximately one-fifth of global greenhouse gas emissions (Nordin et al., 2024). In this context, biomass-derived fuels such as biohydrogen, bioethanol, and biodiesel are recognized as promising energy sources to address climate change (Shweta et al., 2024). Although the use of such fuels is not recent; it dates to 1900, when the diesel engine was invented and powered by peanut oil (Deora et al., 2022).

Specifically, biodiesel, which has proven to be compatible with diesel engines without the need for modifications, is primarily produced through a catalyzed reaction involving the transesterification of triglycerides with short-chain alcohols such as methanol, resulting in fatty acid methyl esters, commonly known as FAME (Pandey et al., 2024). Nevertheless, despite technological advances and efforts to improve biodiesel production processes, the industry continues to face limitations. Some of the most significant challenges in transesterification include the choice and performance of the catalyst, as well as the process required to remove it from the reaction medium (Asaad et al., 2024). Homogeneous catalysts such as NaOH, while highly efficient, lead to excessive generation of wastewater due to the multiple washing required at the end of the reaction (Tan et al., 2019).

On the other hand, heterogeneous catalysts such as metal oxides or mesoporous silicas are easier to separate and have the added advantage of being regenerable and reusable over several reaction cycles (Mashamba et al., 2025). However, their recovery involves separation techniques that demand additional energy, time, and cost in the biodiesel production process (Hua et al., 2025).

Under this scenario, a possible solution to the aforementioned limitations is the use of catalysts with magnetic properties, which allow for easy and rapid removal from the reaction medium and offer potential for reuse (Wang et al., 2025). Nevertheless, a major challenge associated with these catalysts modified with magnetite (Fe_3O_4) is their susceptibility to oxidation when exposed to environmental conditions (de Oliveira et al., 2025). As a result, their catalytic activity and magnetic properties are affected due to the oxidation of Fe^{2+} to Fe^{3+} , leading to the transformation of Fe_3O_4 into $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) (Pincella et al., 2024). Additionally, when magnetite is used directly as a catalyst, there is a risk of iron leaching into the reaction medium, which may remain in the final product (Baldo et al., 2025). One strategy to address this issue is the use of supports, as well as agents that delay oxidation (Mazarío et al., 2024). These strategies help preserve the functionalization of the catalyst over extended periods, enabling the production of large-volume batches that can be stored and used

over several months, thereby reducing the need for frequent catalyst acquisition and minimizing economic losses (Alotaibi et al., 2025; dos Santos et al., 2025).

Among the supports used in catalyst preparation, carbon-based materials derived from biomass or waste stand out, aiming to provide a second use and promote a circular economy, as reported in the studies of Goh et al. (2021), Wang et al. (2024), and Xia et al. (2024), who used palm kernel shells, sugarcane straw, and waste from sargassum and snail shells to prepare magnetic catalysts for biodiesel production, with which they achieved FAME formation percentages of up to 99.43, 99.89 and 99.21 %, respectively, that were able to be used in more than 4 cycles.

Therefore, considering waste valorization and the preservation of the functionality of magnetic catalysts, this study proposes the use of cigarette filter waste and the incorporation of ethylenediaminetetraacetic acid (EDTA) for the preparation and evaluation of materials with magnetic properties through hydrothermal carbonization. This is due to the fact that cigarette filters have become one of the most frequent and persistent types of waste worldwide, mainly due to their improper disposal and indiscriminate discarding in the natural environment (Pietrelli et al., 2025). An alarming fact highlights that of the approximately 6.5 trillion cigarettes consumed each year, around 66% of the butts are thrown into the environment (Fathi et al., 2024). Beyond their visual impact on natural spaces, these cigarette butts represent a serious public health issue, as they release toxic substances adsorbed during tobacco combustion, contaminating soil and water (Motlagh et al., 2024). On the other hand, EDTA is a chelating agent widely used in the synthesis of materials, especially adsorbents, due to its ability to form stable complexes with metal ions, improve the dispersion of metallic species, and generate a strong interaction between the metal and the support (Karimi et al., 2024).

In this context, the main factors affecting the catalytic performance of the resulting materials were evaluated, and a comparison was made between the materials without EDTA functionalization and those functionalized with this agent. Additionally, their behavior over a defined period was analyzed to verify their functionality after that interval.

4.2 Methodology

4.2.1 Hydrothermal preparation of magnetic catalysts from cigarette filter waste

Before the preparation of the materials, the collected cigarette filters were manually cleaned to remove the wrapping paper, tobacco residues, and ash. They were then bleached with a NaOH solution (1% w/v) at 80 °C for 1 hour, followed by repeated washing with boiling deionized water. Subsequently, the filters were dried at 100 °C.

For the preparation of the first nine magnetic catalysts (hereafter referred to as 1-CA/Fe₃O₄ to 9-CA/Fe₃O₄), a one-step hydrothermal carbonization method was employed, using cellulose acetate

obtained from cigarette filter waste as the support, through the application of a Taguchi L₉ experimental design. The preparation involved placing cellulose acetate (1, 2, or 3 g), 3 g of NaOH dissolved in 10 mL of deionized water, and FeCl₃/FeCl₂ metal salts in molar ratios of 1:1, 1:2, or 2:1 (previously dissolved) into a Teflon-lined autoclave. The reactor was then heated in an oven at 180, 200, or 220 °C for 6, 9, or 12 h, according to the combinations established in the Taguchi L₉ (3⁴) experimental design (see Table 4.1). After the hydrothermal carbonization process, each material was dried at 100 °C overnight. Subsequently, the materials were washed with deionized water until reaching a constant pH and then subjected to a second drying under the same conditions.

Table 4.1 Taguchi L₉ experimental design used for the preparation of magnetic catalysts via hydrothermal without EDTA

<i>Catalyst</i>	<i>T, °C</i>	<i>t, h</i>	<i>Amount of cigarette filters, g</i>	<i>FeCl₃/FeCl₂ molar ratio</i>
1-CA/Fe ₃ O ₄	180	6	1	1/1
2-CA/Fe ₃ O ₄		9	2	1/2
3-CA/Fe ₃ O ₄		12	3	2/1
4-CA/Fe ₃ O ₄	200	6	2	2/1
5-CA/Fe ₃ O ₄		9	3	1/1
6-CA/Fe ₃ O ₄		12	1	1/2
7-CA/Fe ₃ O ₄	220	6	3	1/2
8-CA/Fe ₃ O ₄		9	1	2/1
9-CA/Fe ₃ O ₄		12	2	1/1

A second Taguchi L₉ experimental design was carried out to prepare magnetic catalysts with a fixed EDTA concentration (named 1-CA/Fe₃O₄-EDTA[0.2M] to 9-CA/Fe₃O₄-EDTA[0.2M]). The variables used in the previously described design were employed, with the addition of 2 mmol of EDTA in each preparation. However, the influence of EDTA concentration on the catalytic stability of the magnetic materials over time was also evaluated. For this purpose, a Taguchi L₉ (3⁴) experimental design was proposed (see Table 4.2), fixing the amount of cigarette filters (1 g) and considering the amount of EDTA (1, 2, or 3 mmol) as a variable. The materials (1-CA/Fe₃O₄-EDTA to 9-CA/Fe₃O₄-EDTA) were evaluated on day 1, and subsequently on days 30, 60, and 90 after their preparation (see Figure 4.1).

4.2.2 Catalytic evaluation of magnetic materials in the transesterification of soybean oil with methanol

All materials were evaluated as catalysts in the transesterification of soybean oil with methanol, using an oil/methanol molar ratio of 1/30, a catalyst loading of 5 wt% relative to the oil, at 60 °C for 5 h. At the end of the reaction, the catalyst was recovered by magnetic separation. The liquid samples,

after removing the excess methanol, were quantified by gas chromatography using a Thermo Scientific Trace 1300 GC model and methyl heptadecanoate as the internal standard, in accordance with the European standard EN 14103.

Table 4.2 Taguchi L₉ experimental design used for the preparation of magnetic catalysts via hydrothermal with EDTA

Catalyst	<i>T</i> , °C	<i>t</i> , h	Amount of cigarette filters, g	FeCl ₃ /FeCl ₂ molar ratio
1-CA/Fe ₃ O ₄ -EDTA[0.2 M]	180	6	1	1/1
2-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	2	1/2
3-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	3	2/1
4-CA/Fe ₃ O ₄ -EDTA[0.2 M]	200	6	2	2/1
5-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	3	1/1
6-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	1	1/2
7-CA/Fe ₃ O ₄ -EDTA[0.2 M]	220	6	3	1/2
8-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	1	2/1
9-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	2	1/1

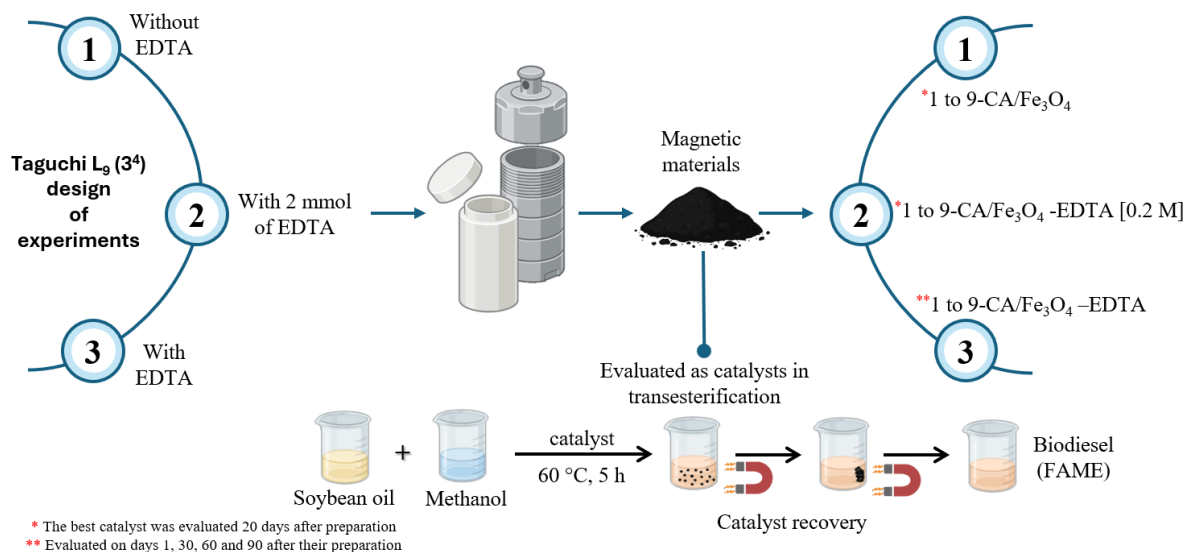


Figure 4.1 Methodology used in the preparation of magnetic catalysts

The quantification results were used in Equation 4.1 to determine the percentage of FAME formation.

$$\% \text{ FAME} = \left(\frac{\sum A_T - A_S}{A_S} \right) \cdot \left(\frac{C_S \cdot V_S}{m} \right) \cdot 100 \quad 4.1$$

where $\sum A_T$: total area including the areas of the FAME; A_S : peak area of the internal standard; C_S : concentration of the standard, mg/mL; V_S : volume of the standard, mL; m : mass of the sample, mg.

The statistical analysis of the experimental design was carried out using MiniTab® software, by calculating the signal-to-noise (S/N) ratio, considering FAME formation as the response variable using Equation 4.2. The "bigger is better" approach was used, since the objective was to maximize the catalytic performance of the materials. This analysis allowed the identification of the impact of the evaluated preparation variables and the establishment of the optimal synthesis conditions.

$$\frac{S}{N} = -10 \log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{x_i^2} \right] \quad 4.2$$

On the other hand, using the material that showed the best catalytic activity 90 days after its preparation (according to the statistical analysis of the experimental design), the optimal reaction conditions (catalyst percentage and soybean oil/methanol molar ratio) were determined through the implementation of a full factorial design. Each reaction was performed in duplicate at 60 °C for 5 h.

Finally, with that catalyst and the optimal reaction conditions determined, kinetic studies were conducted at 40, 50, and 60 °C. Based on these studies, the rate constants for the transesterification reaction were calculated by applying pseudo-first-order and pseudo-second-order models, as indicated in Equations 4.3 and 4.4, respectively.

$$-\ln(1 - X_{ME}) = k_1 t \quad 4.3$$

$$\frac{X_{ME}}{1 - X_{ME}} = k_2 t \quad 4.4$$

where X_{ME} : conversion of triglycerides to fatty acid methyl esters; k_1 : reaction rate constant, min^{-1} ; $k_2 = k'C_{T0}C_{M0}$: reaction rate constant, $\text{L mol}^{-1} \text{min}^{-1}$; t : time, min

The activation energy (E_a , kJ/mol) was also calculated using linear regression analysis based on the Arrhenius equation (4.5).

$$k = Ae^{-\frac{E_a}{RT}} \quad 4.5$$

where A : frequency factor; R : universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

4.2.3 Evaluation of catalyst reusability

The reusability of the best catalyst was evaluated by performing consecutive reactions (under the previously determined optimal conditions), using the same material washed before each cycle. For this purpose, at the end of each reaction cycle, over a total of eight cycles, the magnetic catalyst was

recovered using a magnet, which allowed for quick separation without material loss. The catalyst was then subjected to three consecutive washes with 20 mL of methanol to remove polar compounds, followed by a fourth wash with 20 mL of hexane to eliminate non-polar residues. Once the washing process was completed, the catalyst was dried in an oven at 60 °C for 18 h to ensure proper conditioning before reusing. The reaction product was quantified by gas chromatography, following the methodology described in section 4.2.2.

4.2.4 Physicochemical characterization of the catalysts

X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) techniques were used to identify the crystalline phases, and functional groups present in the best, worst, and intermediate-performing catalysts, prepared with different EDTA concentrations. The samples were analyzed on day 1 and on day 90 after their preparation. Additionally, diffractograms and spectra corresponding to the magnetite obtained under the conditions used for each catalyst were recorded.

4.3 Results and discussion

4.3.1 Performance of the magnetite catalysts

The first materials evaluated as catalysts in the transesterification of soybean oil with methanol were the magnetic materials prepared without EDTA by hydrothermal carbonization. The material 5-CA/Fe₃O₄ showed the best catalytic activity, achieving a FAME formation percentage of 99.81% (see Table 4.3).

Table 4.3 Percentages of FAME formation obtained with magnetic materials prepared via hydrothermal without EDTA

<i>Catalyst</i>	<i>T, °C</i>	<i>t, h</i>	<i>Amount of cigarette filters, g</i>	<i>FeCl₃/FeCl₂ molar ratio</i>	<i>FAME, %</i>
1-CA/Fe ₃ O ₄	180	6	1	1/1	24.98
2-CA/Fe ₃ O ₄		9	2	1/2	16.51
3-CA/Fe ₃ O ₄		12	3	2/1	98.28
4-CA/Fe ₃ O ₄	200	6	2	2/1	16.58
5-CA/Fe₃O₄		9	3	1/1	99.81
*5-CA/Fe₃O₄					71.65
6-CA/Fe ₃ O ₄	220	12	1	1/2	99.64
7-CA/Fe ₃ O ₄		6	3	1/2	92.84
8-CA/Fe ₃ O ₄		9	1	2/1	54.68
9-CA/Fe ₃ O ₄		12	2	1/1	97.20

* Evaluated on day 20 after its preparation; T: temperature t: time

Statistical analysis demonstrated that the hydrothermal carbonization time was one of the variables that most influenced the FAME formation percentage, since the materials that stood out for showing

high catalytic activity were 3, 5, 6, and 9, where it can be seen that, in general, a longer residence time together with a higher temperature resulted in higher conversion (see Table 4.4). This was confirmed by the signal-to-noise ratio analysis, which suggested that it is better to use a temperature of 220 °C and a time of 12 h (see Figure 4.2).

Table 4.4 Analysis of variance of the Taguchi L₉ (3⁴) design of experiments for the preparation of magnetic materials via hydrothermal without EDTA

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>Impact level</i>
Hydrothermal carbonization temperature, °C	82.16	41.08	3
Hydrothermal carbonization time, h	121.01	60.50	2
Amount of cigarette filters, g	134.36	67.18	1
FeCl ₃ /FeCl ₂ molar ratio	6.60	3.30	4
Total	344.15		

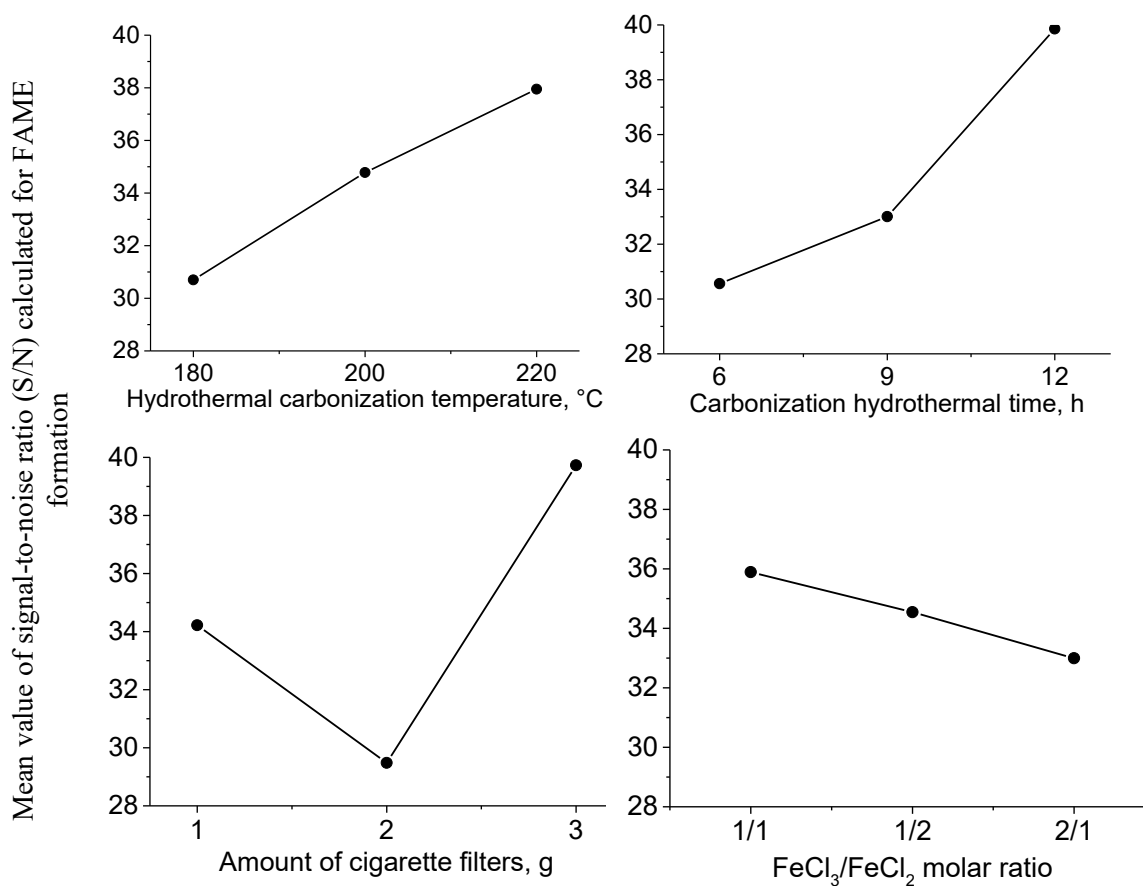


Figure 4.2 S/N ratio analysis of the Taguchi L₉ (3⁴) design of experiments used in the preparation of magnetic catalysts via hydrothermal without EDTA.

The material 5-CA/Fe₃O₄, which initially showed the highest FAME formation percentage, was reevaluated in the transesterification of soybean oil with methanol 20 days after its preparation. In this second evaluation, a decrease of 28.16% in FAME formation was observed, attributed to the oxidation of magnetite (Fe₃O₄) to maghemite (γ -Fe₂O₃) after exposure to ambient oxygen. This is due to the rapid oxidation process of magnetite (Fe₃O₄) to maghemite (γ -Fe₂O₃) upon exposure to oxygen present in the environment, causing the oxidation of Fe²⁺ to Fe³⁺ during this process, as reported by Pincella et al. (2024). This highlights the importance of controlling the degree of oxidation of this compound, since, as mentioned by Orozco-Henao et al. (2024), its magnetic properties are compromised, affecting its functionality, in this case as a catalyst that can be easily recovered using an external magnetic field.

Therefore, to counteract this issue, the materials were prepared again and functionalized with EDTA, a chelating agent that stabilizes iron ions, preventing their oxidation not only during their use in transesterification reactions but also during the preparation process. The results of these materials are shown in Table 4.5.

Table 4.5 Percentages of FAME formation obtained with magnetic materials prepared via hydrothermal with EDTA

<i>Catalyst</i>	<i>T, °C</i>	<i>t, h</i>	<i>Amount of cigarette filters, g</i>	<i>FeCl₃/FeCl₂ molar ratio</i>	<i>FAME, %</i>
1-CA/Fe₃O₄-EDTA[0.2 M]	180	6	1	1/1	96.66
*1-CA/Fe₃O₄-EDTA[0.2 M]					95.54
2-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	2	1/2	92.24
3-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	3	2/1	94.50
4-CA/Fe ₃ O ₄ -EDTA[0.2 M]	200	6	2	2/1	36.07
5-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	3		29.35
6-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	1		28.23
7-CA/Fe ₃ O ₄ -EDTA[0.2 M]	220	6	3	1/2	18.24
8-CA/Fe ₃ O ₄ -EDTA[0.2 M]		9	1	2/1	31.77
9-CA/Fe ₃ O ₄ -EDTA[0.2 M]		12	2	1/1	15.94

* Evaluated on day 20 after its preparation; T: temperature; t: time

Since the material retained its catalytic activity, new materials were prepared with the aim of determining the amount of EDTA required to maintain catalyst stability for up to 90 days (see Table 4.6). With the prepared materials, FAME formation percentages higher than 40% were obtained on the first day. However, only 3 of the 9 materials (2, 3, and 7- CA/Fe₃O₄-EDTA) showed percentages above 90%, whose catalytic activity remained practically stable, as the FAME formation percentages decreased by only 1.7–5.7% after 90 days of preparation.

Table 4.6 Percentages of FAME formation obtained with magnetic materials with EDTA evaluated at different preparation times

<i>Catalyst</i>	<i>Preparation conditions</i>				<i>FAME, %</i>			
	<i>T, °C</i>	<i>t, h</i>	<i>EDTA, mmol</i>	<i>FeCl₃/FeCl₂ molar ratio</i>	<i>Day 1</i>	<i>Day 30</i>	<i>Day 60</i>	<i>Day 90</i>
1-CA/Fe ₃ O ₄ -EDTA	180	6	1	1/1	47.93	32.48	26.80	22.01
2-CA/Fe ₃ O ₄ -EDTA		9	2	1/2	94.17	92.02	91.16	91.09
3-CA/Fe ₃ O ₄ -EDTA		12	3	2/1	90.95	89.06	87.17	85.23
4-CA/Fe ₃ O ₄ -EDTA	200	6	2	2/1	89.12	82.69	80.91	74.80
5-CA/Fe ₃ O ₄ -EDTA		9	3	1/1	40.72	37.88	26.41	24.58
6-CA/Fe ₃ O ₄ -EDTA		12	1	1/2	44.72	31.38	15.80	8.82
7-CA/Fe ₃ O ₄ -EDTA	220	6	3	1/2	99.26	97.99	97.31	97.49
8-CA/Fe ₃ O ₄ -EDTA		9	1	2/1	40.96	35.18	16.22	10.94
9-CA/Fe ₃ O ₄ -EDTA		12	2	1/1	43.49	41.78	40.58	37.69

The analysis of variance from the Taguchi design of experiments on day 1 (see Table 4.7) showed that the amount of EDTA had the greatest impact on the response variable, followed by the FeCl₃/FeCl₂ molar ratio and the hydrothermal carbonization temperature, while time had the least impact.

Table 4.7 Analysis of variance of the Taguchi L₉ (3⁴) design of experiments to evaluate the catalysts on day 1 of their preparation

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>Impact level</i>
Hydrothermal carbonization temperature, °C	12.62	6.31	3
Hydrothermal carbonization time, h	10.30	5.15	4
EDTA, mmol	82.23	41.12	1
FeCl ₃ /FeCl ₂ molar ratio	47.04	23.52	2
Total	152.19		

This is explained because EDTA acts as a complexing agent for iron ions, controlling both the nucleation and growth of magnetite particles. In this way, an adequate amount of EDTA ensures smaller, better dispersed particles with more uniform interaction with the carbon structure, thus improving catalytic performance (Nedylakova et al., 2024). The molar ratio also played a decisive role in the formation of methyl esters of fatty acids, as it determines the formation of pure magnetite or the formation of secondary phases, which in turn determine catalytic efficiency (Ajinkya et al., 2020). The hydrothermal carbonization temperature showed a minor effect, although it still influences the crystallization and formation of the structure, which favors the development of particles with better crystal order (Silva et al., 2023). The carbonization time was the variable with the least impact,

indicating that, within the evaluated range, the treatment duration was sufficient to complete the nucleation and growth of the particles, so increasing the process time would not provide significant improvements in the result (Cursaru et al., 2020). Therefore, the signal-to-noise ratio analysis, shown in Figure 4.3, suggested that the levels that improve the percentage of FAME are 180 °C, 6 h, and a molar ratio of $\text{FeCl}_3/\text{FeCl}_2$ of 1/2 with 2 or 3 mmol of EDTA. To save reagents and, consequently, reduce the production cost, the amount of 2 mmol would be considered.

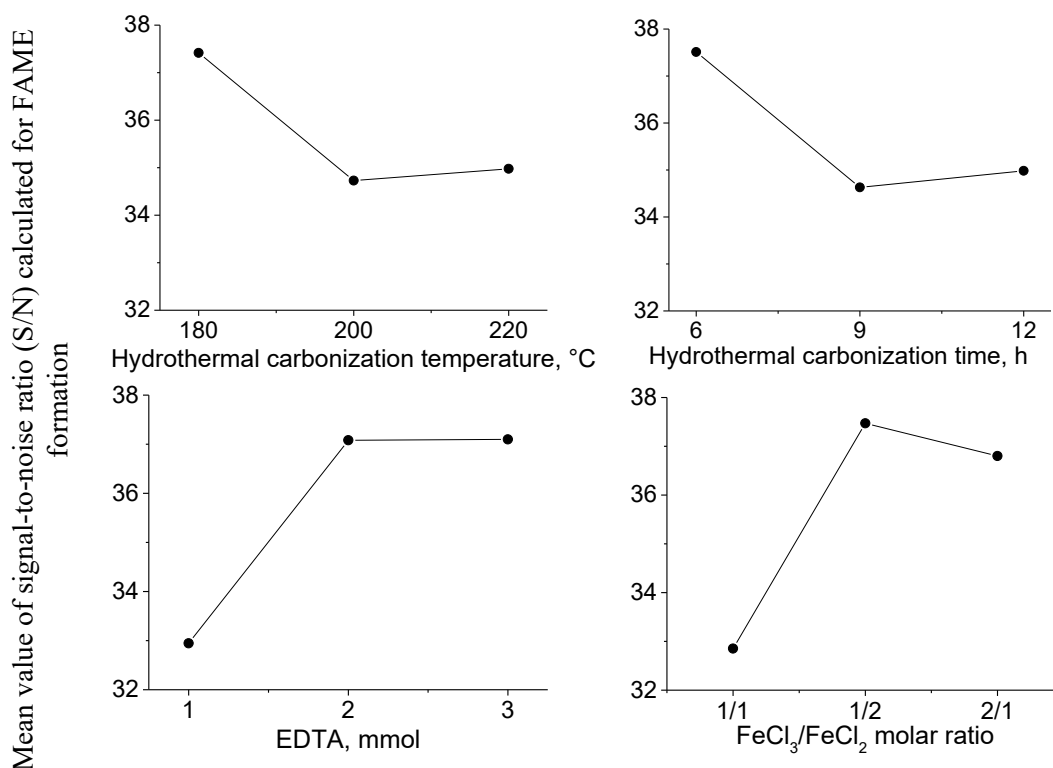


Figure 4.3 S/N ratio analysis of the Taguchi $L_9(3^4)$ design of experiments to evaluate the catalysts on day 1 of their preparation

It should be noted that when the molar ratio of iron chlorides deviates too much towards Fe^{3+} , the formation of secondary phases (maghemite or hematite) is favored, which exhibit lower magnetization and lower catalytic performance. If the excess is too much towards Fe^{2+} , amorphous phases with low stability and reduced activity may occur. Therefore, although the theoretical balance is 2/1, the results of the Taguchi design suggested that an inverse relationship (1/2 with excess Fe^{2+}) favors catalytic activity. This may be due to the use of EDTA, which, by binding with Fe^{3+} , allows its immediate availability to participate in nucleation to be reduced, generating a reward effect, balancing the system and allowing more controlled and balanced formation of Fe_3O_4 , as mentioned by Jungcharoen et al. (2023).

However, the level of impact of the factors changed depending on the time at which the materials were evaluated, as after 90 days the amount of EDTA showed the greatest impact, followed by temperature, carbonization time, and the $\text{FeCl}_3/\text{FeCl}_2$ molar ratio (see Table 4.8).

Table 4.8 Analysis of variance of the Taguchi L_9 (3^4) design of experiments to evaluate the catalysts on day 90 after preparation

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>Impact level</i>
Hydrothermal carbonization temperature, °C	72.40	36.20	2
Hydrothermal carbonization time, h	58.61	29.30	3
EDTA, mmol	388.34	194.17	1
$\text{FeCl}_3/\text{FeCl}_2$ molar ratio	26.75	13.37	4
Total	546.08		

Nevertheless, the signal-to-noise ratio analysis (see Figure 4.4) yielded the same results as the analysis of variance from the other evaluated days, so the suggested levels remained the same (180 °C, 6 h, $\text{FeCl}_3/\text{FeCl}_2$ ratio of 1/2, and 2 mmol of EDTA).

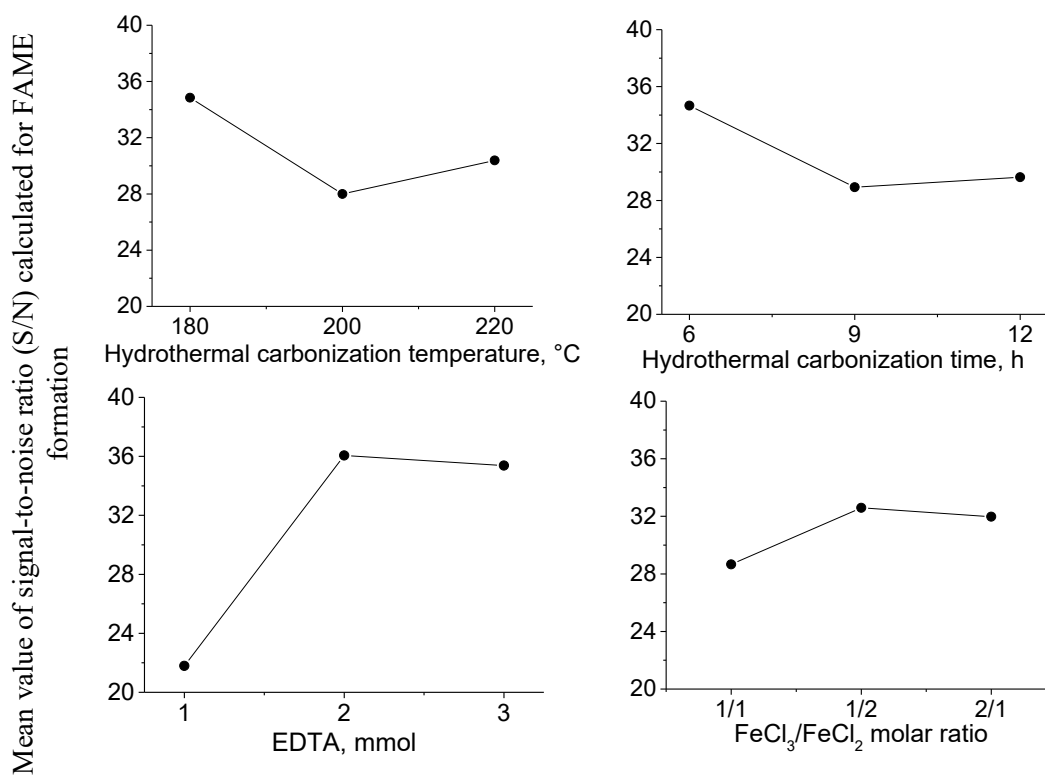


Figure 4.4 S/N ratio analysis of the Taguchi L_9 (3^4) design of experiments to evaluate the catalysts on day 90 after preparation

Therefore, the optimal conditions suggested by the signal-to-noise ratio analysis were considered to prepare a new material (NCA/Fe₃O₄-EDTA) and to determine the reaction conditions that would allow for the highest possible percentage of FAME formation. To achieve this, a full factorial experimental design was implemented, with its details and results presented in Table 4.9.

The results indicated that an increase in the catalyst percentage and a higher molar ratio of soybean oil/methanol lead to a higher percentage of FAME formation, demonstrating that both factors influence the process.

Table 4.9 Full factorial design used to determine transesterification conditions using the NCA/Fe₃O₄-EDTA catalyst

<i>Experimental condition</i>	<i>Catalyst, %</i>	<i>Soybean oil/methanol molar ratio</i>	<i>FAME, %</i>
1	3	1/15	76.88
2		1/18	78.19
3		1/21	83.08
4	5	1/15	99.97
5		1/18	99.95
6		1/21	99.96
7	7	1/15	99.97
8		1/18	99.98
9		1/21	99.97

This is because increasing the amount of catalyst results in a greater availability of active sites, which allows for an increase in reaction speed and efficiency, favoring a greater conversion to fatty acid methyl esters (González et al., 2020). On the other hand, the molar oil/alcohol ratio directly influences the displacement of the chemical equilibrium, so an increase in the amount of methanol displaces the reaction towards the products, due to an improvement in the miscibility between phases, facilitating contact between oil, methanol, and catalyst, which contributes to a greater overall efficiency of the process (Larimi et al., 2024). However, it is important to mention that both excess catalyst and alcohol have limitations. A high amount of catalyst causes problems with agglomeration and an increase in the viscosity of the medium, mainly (Yusuf et al., 2024).

Similarly, excessive alcohol use can complicate product separation and increase production and purification costs (Selvam et al., 2025). These experimental observations are consistent with the analysis of variance, as shown in Table 4.10, where the p-values for both factors and their interaction were below the significance level of 0.05, confirming that the catalyst concentration and the oil-to-methanol molar ratio significantly affect FAME production.

Transesterification condition number 4 was selected, which involves a catalyst concentration of 5 wt% with respect to the oil and a soybean oil/methanol molar ratio of 1/15. These conditions allow

achieving the maximum possible percentage of FAME formation with a reduced amount of both catalyst and methanol.

Table 4.10 Analysis of variance of the full factorial experimental design used to determine the transesterification conditions using the NCA/Fe₃O₄-EDTA catalyst

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>p-value</i>
Catalyst, %	1694.41	847.20	4x10 ⁻¹⁵
Soybean oil/methanol molar ratio	14.19	7.09	6.3x10 ⁻⁶
Interaction Catalyst, % - Soybean oil/methanol molar ratio	28.55	7.13	1.7x10 ⁻⁶
Error	1.07	0.11	
Total	1738.23		

With the determined transesterification conditions and the previously mentioned catalyst (obtained at 180 °C, 6 h, and a FeCl₃/FeCl₂ molar ratio of 1/2 with 2 mmol of EDTA), reaction kinetics were carried out at 40, 50, and 60 °C, the results of which are shown in Figure 4.5.

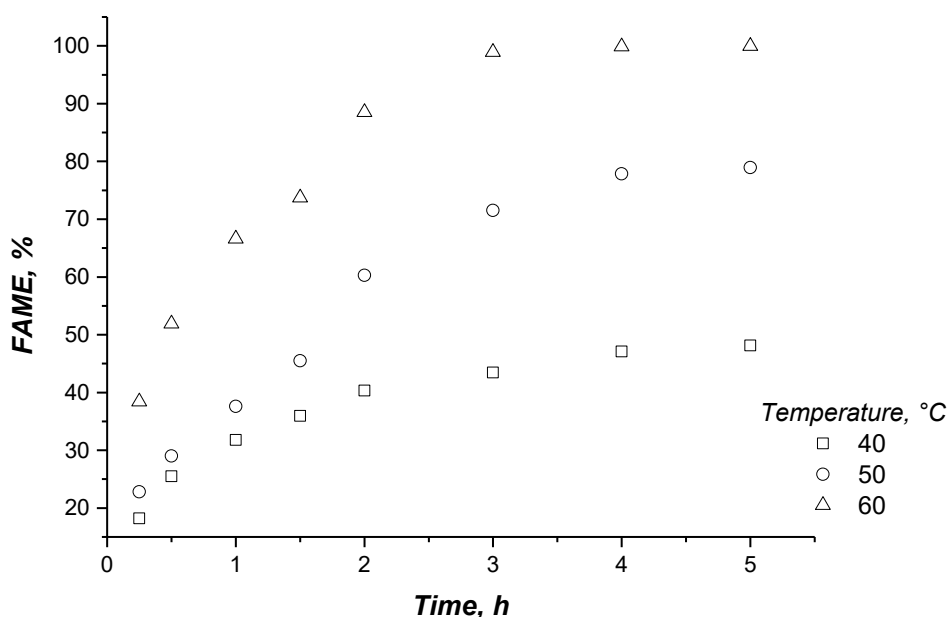


Figure 4.5 Transesterification kinetics of soybean oil obtained with 5% catalyst and a 1/15 molar ratio using the NCA/Fe₃O₄-EDTA catalyst

The transesterification kinetics were fitted to the pseudo-first-order and pseudo-second-order models, and the reaction rate constants and determination coefficients (R^2) shown in Table 4.11 were obtained. It was observed that increasing the temperature speeds up the reaction, as the rate constants increase and the time needed to reach maximum conversion is reduced. At 40 °C, a conversion of

48.12% was obtained after 5 hours of reaction, while at 60 °C, a conversion of 98.92% was achieved in just 3 hours. This means that, at low temperatures, the reaction proceeds slowly because the molecules do not have enough energy to overcome the activation barrier. As the temperature increases, the kinetic energy of the molecules also increases, raising the frequency of collisions and accelerating the conversion to biodiesel, thus demonstrating that the process is endothermic (Ghosh et al., 2025).

Table 4.11 Rate constants and coefficients of determination obtained with kinetic models for the transesterification of soybean oil

Temperature, °C	k_1, min^{-1}	$k_2, \text{L mol}^{-1} \text{min}^{-1}$	$R^2, \text{pseudo first order}$	$R^2, \text{pseudo second order}$	$E_a, \text{kJ/mol}$
40	0.0031	0.0045	0.46	0.67	81.31
50	0.0071	0.0122	0.93	0.97	
60	0.0203	0.0422	0.96	0.96	

Statistically, it was determined that the pseudo-second-order model was the most suitable to describe the experimental data, with R^2 values ranging from 0.67 to 0.97. Additionally, the activation energy (E_a) required to carry out the transesterification of soybean oil was determined to be 81.31 kJ/mol, which falls within the range (34–83.9 kJ/mol) reported by Maleki and Talesh (2024), indicating that the reaction is heterogeneous and chemically controlled.

On the other hand, the evaluation of the catalyst reuse was carried out under the same conditions used in the transesterification kinetic study, setting the temperature at 60 °C. The results obtained for each cycle are shown in Figure 4.6.

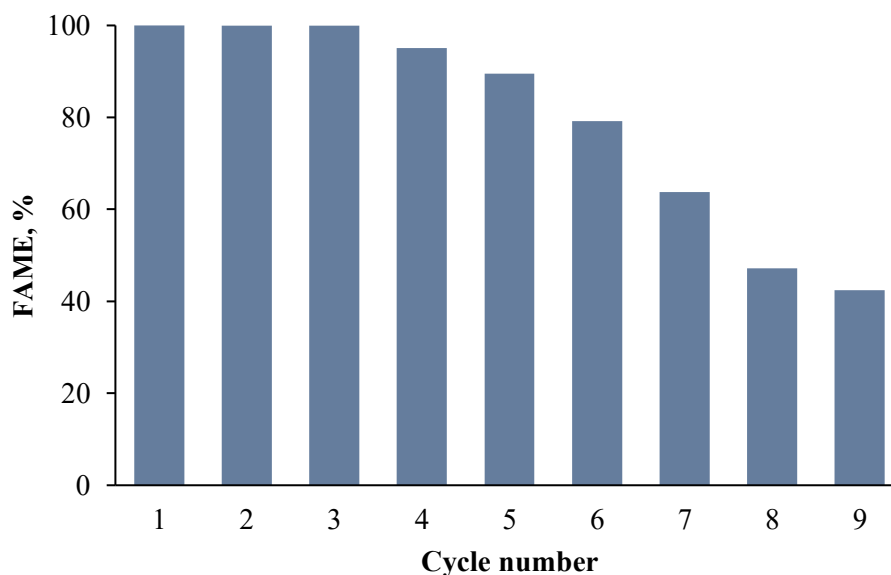


Figure 4.6 Reusability of the magnetic catalyst NCA/ Fe₃O₄-EDTA

It was observed that the material (NCA/Fe₃O₄-EDTA) maintained its catalytic activity up to the third cycle, reaching a FAME formation of 99.7%. From the fourth cycle onward, a 4.89% decrease was observed compared to the first cycle, progressively declining to 42.43% by the ninth cycle. This decrease in biodiesel production could be attributed to the deactivation of the catalyst active sites, possibly caused by the accumulation of unreacted oil, biodiesel, or even glycerol residues that could not be removed during the washing process, as mentioned by Islam et al. (2022).

4.3.2 Physicochemical characterization of the EDTA-functionalized magnetic catalysts

Catalysts 6 and 7-CA/Fe₃O₄-EDTA of the experimental design showed in Table 4.6, which exhibited the lowest and highest FAME formation percentages, respectively, were characterized by XRD and FTIR. Additionally, the catalyst with an intermediate FAME formation percentage, 9-CA/Fe₃O₄-EDTA, was also characterized.

Regardless of the preparation conditions, the XRD diffractograms (Figure 4.7) of the iron oxide (magnetite) showed consistent peaks at 18.3, 30.2, 35.3, 37.0, 43.2, 53.5, and 57.3° 2 θ , corresponding to the crystalline structure of this compound (da Silva et al., 2023). These peaks were observed in the diffractograms of the samples from the three catalysts processed immediately after their preparation (Day 1), thus confirming the presence of the magnetic compound in the obtained materials. In contrast, the diffractograms of the aged catalyst samples (90 days) showed peaks of lower intensity and even the absence of two peaks, those located at 18.3 and 37.08° 2 θ . However, the most intense characteristic peaks of magnetite remained, observed at 30.2, 35.3, 43.2, and 57.3° 2 θ .

Likewise, the FTIR spectra (see Figure 4.8) confirmed the presence of magnetite in the materials, as they displayed the characteristic Fe–O vibration band located at 584 cm⁻¹ (Chong et al., 2024), although with lower intensity than that of the pure compound. The appearance of a band located at 3400 cm⁻¹ was also observed in the catalysts, both in the fresh and aged samples. This band is associated with the stretching of the O–H group (Shao et al., 2024), possibly due to the use of cellulose acetate in the preparation of the materials.

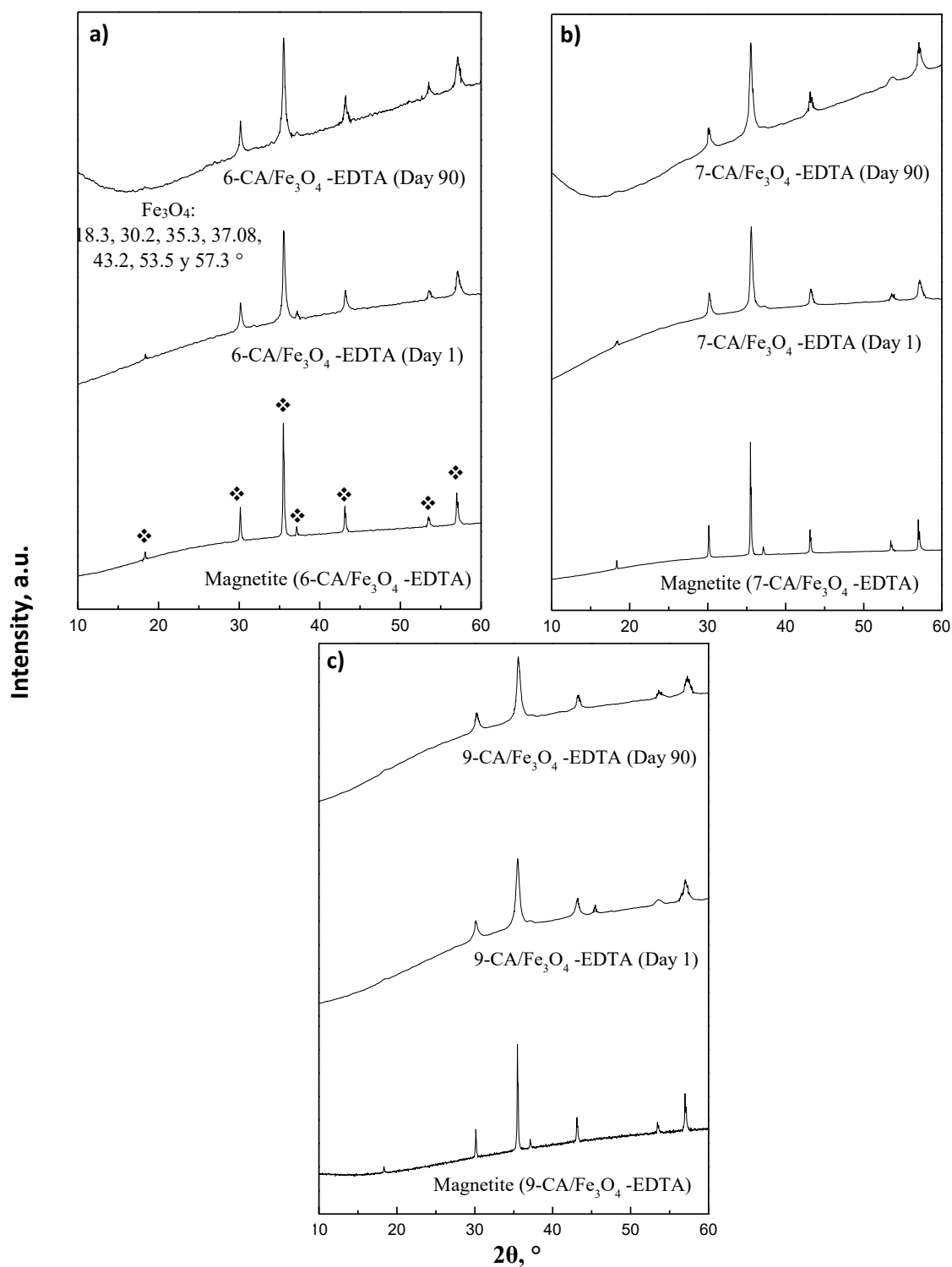


Figure 4.7 XRD diffractograms of a) Catalyst 6-CA/Fe₃O₄-EDTA; b) Catalyst 7-CA/Fe₃O₄-EDTA and c) Catalyst 9-CA/Fe₃O₄-EDTA on day 1 and 90 of their preparation, as well as the magnetite prepared under the conditions of each catalyst

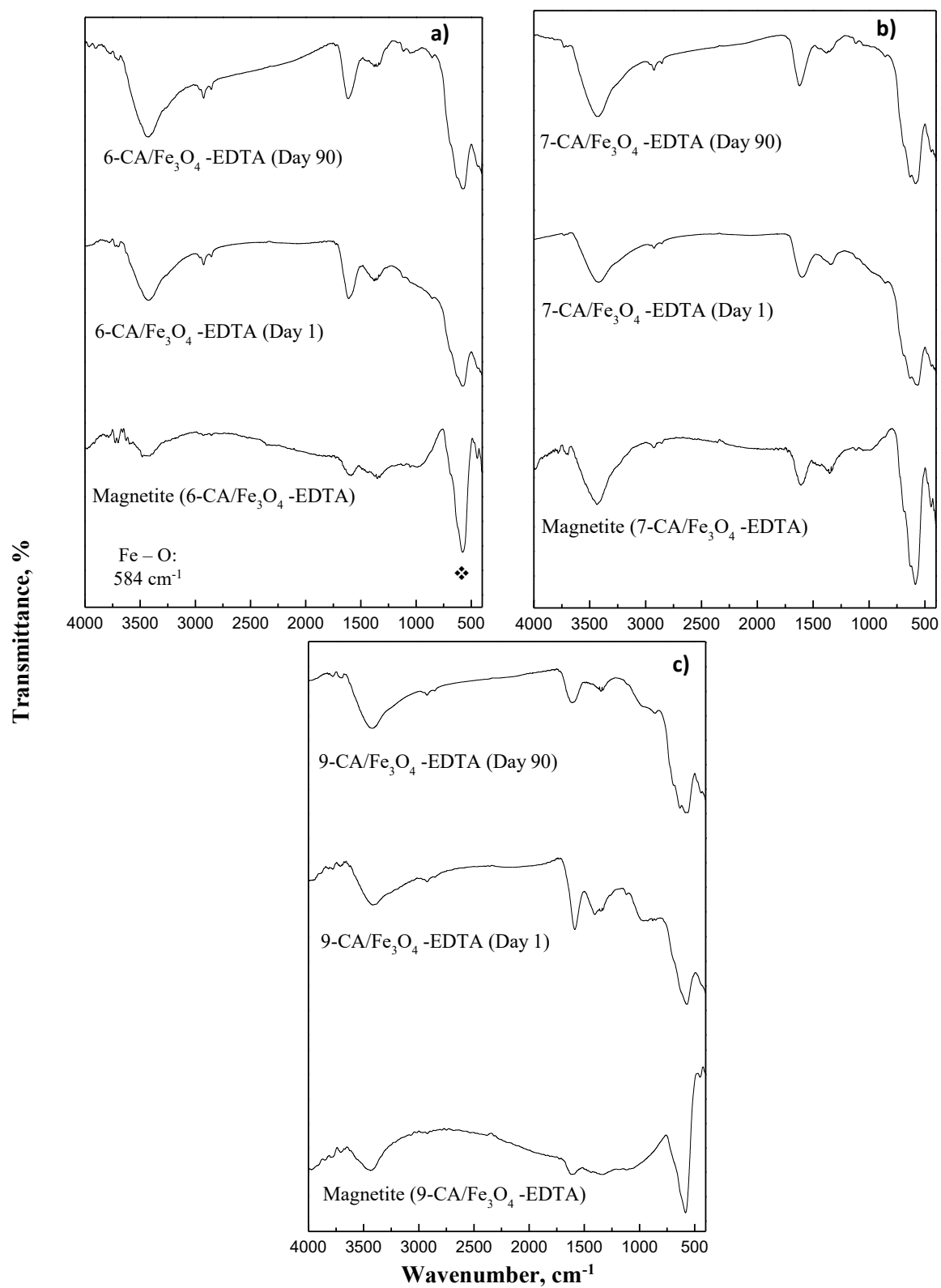


Figure 4.8 FTIR spectra of a) Catalyst 6; b) Catalyst 7 and c) Catalyst 9 on days 1 and 90 of their preparation, as well as the magnetite prepared under the conditions of each catalyst

4.4 Conclusions

Cigarette filter waste, an abundant and environmentally harmful type of waste, was utilized in the preparation of magnetic catalysts employed in the production of biodiesel from soybean oil. This was achieved through the application of different experimental designs, which enabled the identification of the optimal preparation and reaction conditions to maximize the formation of fatty acid methyl esters. Among the non-functionalized materials, the 5-CA/Fe₃O₄ catalyst achieved percentage of FAME formation of 99.81 %; however, its catalytic activity declined when reevaluated 20 days after its preparation. This decrease in catalytic performance was attributed to the instability of the magnetic compound under normal environmental conditions, which led to the oxidation of magnetite to maghemite. Therefore, it was necessary to stabilize the iron using chelating agents such as EDTA.

The incorporation of EDTA enabled the synthesis of materials with greater stability and catalytic activity, even after 90 days of storage. The catalysts that stood out for maintaining their catalytic performance and achieving percentage of FAME formation above 90% were 2-, 3-, and 7-CA/Fe₃O₄-EDTA. According to the results of variance analysis and signal-to-noise (S/N) ratio analysis, it was determined that using a carbonization temperature and time of 180 °C and 6 h, a FeCl₃/FeCl₂ molar ratio of 1/2, and 2 mmol of EDTA, an efficient and stable material is obtained. With this optimized catalyst (NCA/Fe₃O₄-EDTA), kinetic and reuse studies were conducted, which revealed that the transesterification system was endothermic and chemically controlled. Furthermore, the pseudo-second-order kinetic model best described the experimental data, with R² values ranging from 0.67 to 0.97. In the reuse study, it was shown that the NCA/Fe₃O₄-EDTA catalyst could be reused for up to four cycles while achieving a 95.11 % of FAME.

Additionally, physicochemical characterization confirmed the presence of the magnetic compound in the catalysts, with its main diffraction peaks and bands preserved even after 90 days of preparation.

Therefore, this study demonstrates the potential of magnetic materials derived from cigarette filter waste, especially those functionalized with EDTA, as efficient and stable catalysts for biodiesel production through transesterification. This not only extended the useful life of the catalysts but also added value to a type of waste that commonly lacks a second use.

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Chapter 5. Preparation and catalytic evaluation of magnetic materials derived from EDTA-functionalized and $\text{Ca}(\text{OH})_2$ -modified cigarette filter waste for biolubricant production

Abstract

This chapter presents the synthesis of magnetic catalysts from cigarette filter waste modified with calcium hydroxide, with the aim of improving the production of trimethylolpropane fatty acid esters (FATE), compounds of interest in the synthesis of biolubricants. The catalyst preparation first involved obtaining a magnetic material functionalized with EDTA through hydrothermal carbonization. This material was then modified with calcium hydroxide using a full factorial experimental design to evaluate the effect of calcium nitrate and sodium hydroxide concentrations. The optimal preparation conditions (0.4 M $\text{Ca}(\text{NO}_3)_2$ and 1 M NaOH) produced the highest FATE formation. The catalytic performance was evaluated in the transesterification of biodiesel (produced from soybean oil and methanol) with trimethylolpropane under various reaction conditions. The highest conversion (91.83%) was obtained using 5 wt% catalyst and a biodiesel/TMP molar ratio of 1/1 at 140 °C. Kinetic modeling indicated that the second-order model best described the reaction, with an activation energy of 94.7 kJ/mol. Catalyst reuse was demonstrated for up to five cycles, with a gradual decrease in performance. X-ray diffraction analysis confirmed the presence of magnetite and calcium hydroxide in the catalyst before reaction use, as well as the disappearance and reduction of the characteristic peaks of these compounds after use.

5.1 Introduction

Lubricants are widely used in the industrial and automotive sectors as they enhance the performance of mechanical systems by facilitating movement between parts (Malik et al., 2023). Most lubricants currently in use are derived from petroleum; however, they face several issues such as the future depletion of fossil fuels, rising crude oil prices, and, most importantly, the soil and water pollution they cause during use and disposal (Teshome et al., 2025). Consequently, there has been an increasing demand for more environmentally friendly lubricants that are not petroleum-dependent. This has motivated the development of processes to obtain compounds with properties like or even better than those of conventional lubricants, but that are environmentally benign (Sancheti and Yadav, 2022). Lubricants based on fatty acid trimethylolpropane esters (FATEs) have become popular due to their excellent lubricating properties, biodegradability, and lower toxicity, positioning them as a viable alternative to fossil-based lubricants (Sarma and Vinu, 2022).

Among the methods for obtaining biolubricants, transesterification is one of the most widely used due to its simplicity and the possibility of being part of a continuous double-reaction process. In the first step, biodiesel is obtained from a vegetable oil, which is then used as a reactant in the second reaction to be transesterified with a complex alcohol, in the presence of a catalyst, to produce the corresponding lubricant (Bahadi et al., 2021). One of the main factors influencing the reaction yield is the catalyst. Basic homogeneous catalysts such as KOH or NaOH are commonly used; however, since they are in the same phase as the reaction medium, they are difficult to recover (Pawar and Hulwan, 2025). In this regard, the use of heterogeneous catalysts enables more efficient recovery, resulting in lower production costs, faster processing, and reduced wastewater generation, since no washing steps are required as with homogeneous catalysts (Kibar et al., 2023). Additionally, this allows the catalyst to be regenerated and reused in more than one catalytic cycle (Ghosh and Halder, 2022).

In this context, interest has grown in the use of heterogeneous catalysts, particularly those prepared from low-cost materials such as biomass or waste (Jahromi et al., 2021). Therefore, this study focuses on the preparation of heterogeneous catalysts with magnetic properties from cigarette filter waste, aiming to repurpose this type of urban waste, which currently lacks proper disposal. The materials, obtained via hydrothermal carbonization, were modified with calcium hydroxide to improve the production of FATE through the transesterification of biodiesel with trimethylolpropane.

5.2 Methodology

5.2.1 Hydrothermal preparation of magnetic catalysts from calcium hydroxide-modified cigarette filter waste

The materials were prepared considering a previously developed catalyst that had been evaluated in the transesterification of soybean oil with methanol, which resulted in the maximum conversion of FAME. This material was prepared using 1 g of cigarette filters (which were cleaned and washed prior to use), a molar ratio of $\text{FeCl}_3/\text{FeCl}_2$ of 1/2, 2 mmol of EDTA at 180 °C for 6 hours of hydrothermal carbonization. Subsequently, it was modified with calcium hydroxide. For this purpose, a full factorial experimental design was used, in which the concentrations of calcium nitrate (0.2 to 0.6 M) and sodium hydroxide (0.5 to 1.5 M) were evaluated, as shown in Table 5.1. The preparation consisted of stirring 2 g of magnetic catalyst in a calcium nitrate solution (according to the concentration specified in the experimental design) at 60 °C for 3 hours. Next, the sodium hydroxide solution was added dropwise and stirring continued for another 3 h (see Figure 5.1). Finally, the resulting material was dried at 100 °C for 12 h.

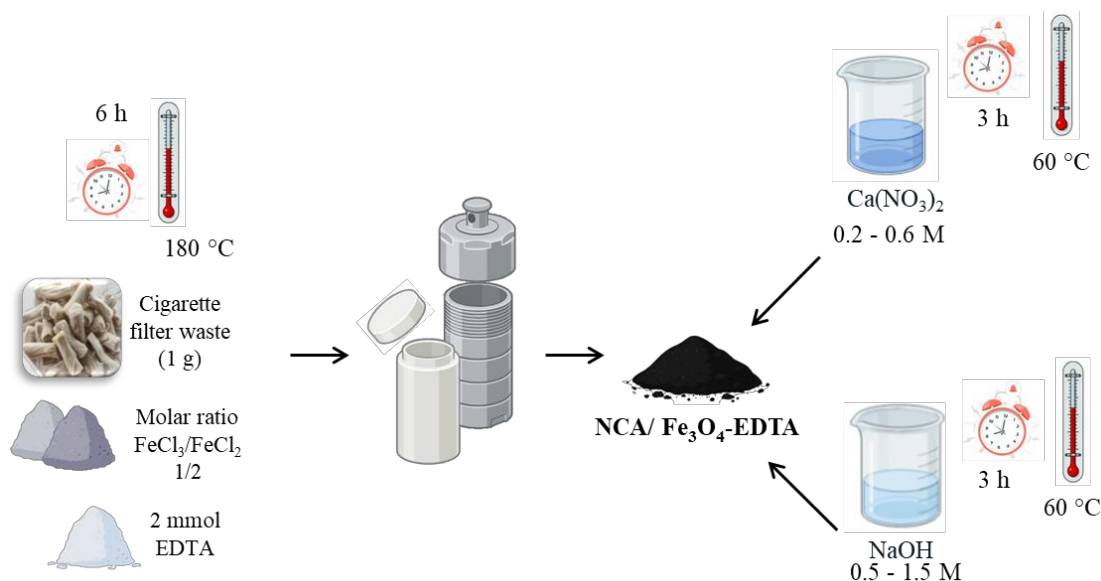


Figure 5.1 Methodology used in the preparation of magnetic materials evaluated in the production of biolubricant

5.2.2 Evaluation of calcium hydroxide-modified magnetic catalysts in FAME transesterification

The catalysts were evaluated in the transesterification of fatty acid methyl esters with trimethylolpropane (TMP). The biodiesel used for this reaction was obtained by transesterification of soybean oil with methanol, using a 1/15 molar ratio and 0.5 g of KOH as catalyst at 60 °C for 5 hours. The reaction in which the catalysts were tested consisted of using 5 wt% of catalyst relative to the

biodiesel mass, with a biodiesel/TMP molar ratio of 3/1 at 140 °C for 5 hours. At the end of the reactions, the material was easily recovered by applying an external magnetic field. The product was quantified using a gas chromatograph following the methodology specified in European standard EN 14103, using methyl heptadecanoate as the internal standard. The quantification results were used in the following equation to determine the percentage of unreacted FAME.

$$\% \text{ FAME} = \left(\frac{\sum A_T - A_S}{A_S} \right) \cdot \left(\frac{C_S \cdot V_S}{m} \right) \cdot 100 \quad 4.1$$

where $\sum A_T$: total area including the areas of the FAME; A_S : peak area of the internal standard; C_S : concentration of the standard, mg/mL; V_S : volume of the standard, mL; m : mass of the sample, mg.

The percentage of FAME formation was then used in a second equation (5.2) to determine the formation of fatty acid trimethylolpropane esters (FATE).

$$\% \text{ FATE} = \% \text{ FAME}_{\text{biodiesel}} - \% \text{ FAME}_{\text{FATE}} \quad 5.2$$

where

$\% \text{ FAME}_{\text{biodiesel}} = \% \text{ FAME}$ present in the biodiesel used in the reaction

$\% \text{ FAME}_{\text{TMP esters}} = \% \text{ unreacted FAME}$

The material that showed the best catalytic performance was used to determine the optimal reaction conditions. Subsequently, with the best catalyst and the optimal reaction conditions, transesterification kinetics were obtained at 140 and 150 °C. Based on the kinetic results, kinetic parameters such as reaction rate constants and activation energy were determined using the following equations described by Menkiti et al. (2016):

$$\ln \frac{[TMP_o]}{[TMP]} = k_1 t \quad 5.3$$

$$\frac{1}{[TMP]} - \frac{1}{[TMP_o]} = k_2 t \quad 5.4$$

where $[TMP_o]$ = initial concentration of TMP, mmol/L; $[TMP]$ = concentration at time t , mmol/L; t = time, min; k_1 = reaction rate constant, min^{-1} ; k_2 = reaction rate constant, $\text{L mol}^{-1} \text{ min}^{-1}$

The activation energy (E_a , kJ/mol) was also calculated using linear regression analysis based on the Arrhenius equation (5.5).

$$k = Ae^{-\frac{E_a}{RT}} \quad 5.5$$

where A : frequency factor; R : universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

5.2.3 Evaluation of catalyst reusability

The reusability of the best catalyst was evaluated by performing consecutive reactions (under the previously determined optimal conditions), using the same material washed before each cycle. For

this purpose, at the end of each reaction cycle, over a total of eight cycles, the magnetic catalyst was recovered using a magnet, which allowed for quick separation without material loss. The catalyst was then subjected to three consecutive washes with 20 mL of methanol to remove polar compounds, followed by a fourth wash with 20 mL of hexane to eliminate non-polar residues. Once the washing process was completed, the catalyst was dried in an oven at 60 °C for 18 hours to ensure proper conditioning before reusing. The reaction product was quantified by gas chromatography, following the methodology described in section 5.2.2.

5.2.4 Physicochemical characterization of the catalyst

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used to identify the crystalline phases present in the best catalyst, in the magnetite and the catalyst used in the last reaction cycle evaluated. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used to identify the crystalline phases and functional groups present in the best catalyst, magnetite, and the catalyst used in the last evaluated reaction cycle. The diffractograms were generated using a Malvern-Panalytical Empyrean diffractometer equipped with a PIXel 1D detector. The samples were analyzed under the following conditions: a speed of 96 s, a step of 0.026°, a scanning range between 10° and 60°, and CuK α 1 radiation of 1.5405 Å. On the other hand, the FTIR spectra were obtained with a Nicolet iS10 Thermo Scientific FT-IR spectrometer. The samples were prepared by dilution in KBr to form pellets, which were analyzed in a wavenumber range of 4000 to 400 cm⁻¹.

5.3 Results and discussion

5.3.1 Performance and evaluation of the magnetite catalysts for FATE production

The results of the full factorial design of experiments are shown in Table 5.1.

Table 5.1 Full factorial design of experiments to determine the preparation conditions that favor the percentage of trimethylolpropane ester formation

<i>Catalyst</i>	<i>[Ca(NO₃)₂], M</i>	<i>[NaOH], M</i>	<i>FATE, %</i>
1	0.2	0.5	50.31
2		1	57.05
3		1.5	58.06
4	0.4	0.5	54.51
5		1	66.43
6		1.5	62.78
7	0.6	0.5	52.01
8		1	52.56
9		1.5	57.08

The results indicated that an increase in the concentration of calcium nitrate and sodium hydroxide to 0.4 and 1 M, respectively, leads to a higher percentage of trimethylolpropane ester formation, which shows that both factors influence this process. This finding was supported by the analysis of variance presented in Table 5.2, where the experimental F-values are higher than the theoretical F-values. In addition, the p-values for both factors and their interaction were below the established significance level of 0.05. Therefore, it can be concluded that both factors have a significant effect on the percentage of TMP ester formation.

Table 5.2 Analysis of variance of the full factorial experimental design used to determine the preparation conditions of the materials

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>F_{exp}</i>	<i>F_{theoretical}</i>	<i>p-value</i>
[Ca(NO ₃) ₂], M	177.04	88.52	783.84	4.25	8x10 ⁻¹¹
[NaOH], M	185.99	92.99	823.45	4.25	6.4x10 ⁻¹¹
Interaction [Ca(NO ₃) ₂], M - [NaOH], M	72.75	18.18	161.05	3.63	2.3x10 ⁻⁸
Error	1.01	0.11			
Total	436.8				

$\alpha=0.05$

Therefore, catalyst number 5 was used to determine the optimal reaction conditions, with the aim of improving FATE production. The results are shown in Table 5.3.

Table 5.3 Full factorial experimental design to determine the best transesterification conditions

<i>Experimental condition</i>	<i>Catalyst, %</i>	<i>Biodiesel/TMP molar ratio</i>	<i>FATE, %</i>
1	5	1/1	91.83
2		2/1	86.70
3		3/1	68.61
4	7.5	1/1	68.59
5		2/1	64.28
6		3/1	61.75
7	10	1/1	58.56
8		2/1	55.67
9		3/1	49.43
10	15	1/1	45.41
11		2/1	42.34
12		3/1	34.76

The results also indicated that a Biodiesel/TMP molar ratio of 1/1 increases the percentage of FATE formation, while the 3/1 molar ratio yielded the lowest percentages. In turn, the catalyst percentage also showed an impact on FATE formation, with 5% catalyst being the most effective.

This effect is possibly since an excess of catalyst may cause darkening of the product due to an oxidation process, which alters both the purity and quality of the esters obtained, as mentioned by Bayryamov and Kopchev, 2022.

The analysis of variance (Table 5.4) confirmed the influence of the evaluated factors, since the p-values were below the established level (0.05) and the experimental F-values were higher than the theoretical F-values for both the individual factors and their interaction.

Table 5.4 Analysis of variance of the full factorial experimental design used to determine the preparation conditions of the materials

<i>Variables</i>	<i>Sum of squares</i>	<i>Variance</i>	<i>F_{exp}</i>	<i>F_{theoretical}</i>	<i>p-value</i>
Catalyst, %	5327.55	1775.85	3145.41	3.49	5×10^{-16}
Biodiesel/TMP molar ratio	687.43	343.71	608.79	3.88	8.6×10^{-13}
Interaction Catalyst,% - Biodiesel/TMP molar ratio	193.01	32.17	56.98	2.99	4×10^{-8}
Error	6.77	0.56			
Total	6214.76				

$\alpha=0.05$

Therefore, with the best catalyst and the best reaction conditions (5% catalyst, biodiesel/TMP molar ratio 1/1) the transesterification kinetics were obtained at 140 and 150 °C, the results of which are shown in Figure 5.2.

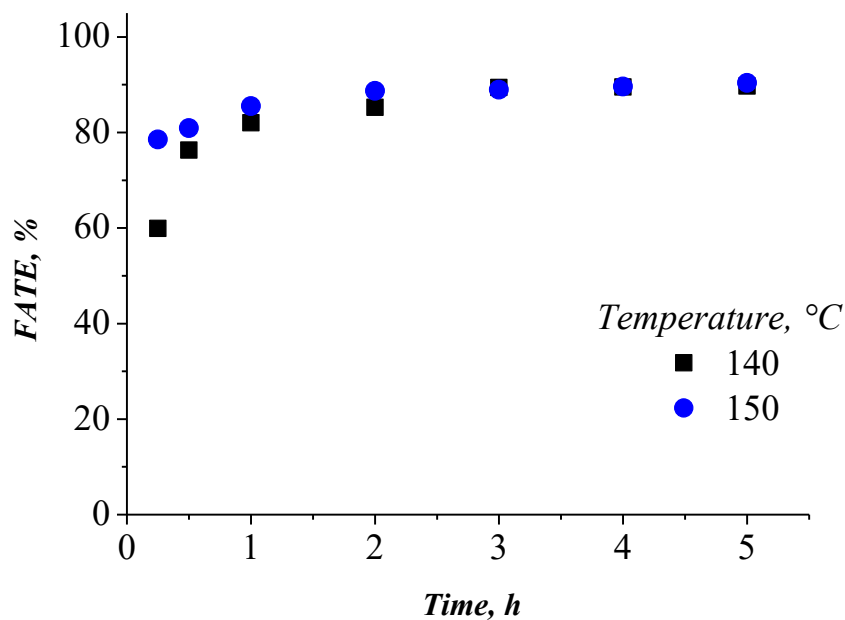


Figure 5.2 Transesterification kinetics of FAME obtained with 5 % catalyst and a 1/1 molar ratio of FAME/TMP using catalyst 5

An increase in temperature was observed to accelerate the reaction rate, promoting a higher conversion of FAME to FATE, which suggests that the reaction is endothermic, as mentioned by Elmelawy et al. (2023). They also indicate that this is due to the increase in temperature that enhances the interaction between the catalyst and the reagents. An 18.59% increase in conversion was observed when comparing FATE formation at 150 °C (78.59%) with that obtained at 140 °C (59.93%) after the first 15 minutes of reaction.

For the kinetic analysis, first- and second-order models were used to obtain rate constants. The coefficient of determination (R^2) was employed as a statistical parameter to identify the model that best fit the experimental results. The results of this modeling are detailed in Table 5.5, with the second-order model providing the best fit to the data, with determination coefficients of 0.97–0.98.

5.3.2 Evaluation of catalyst reusability

The evaluation of catalyst reuse was carried out under the same conditions used in the kinetic study of transesterification at a temperature of 140 °C. The results are shown in Figure 5.3. It was observed that the material gradually lost its catalytic performance; in the first 5 cycles, a gradual decrease of between 2.06% and 4.01% per cycle was recorded, reaching 73.9% in the fifth reaction.

Table 5.5 Rate constants and coefficients of determination obtained with kinetic models for the transesterification of biodiesel for FATE production

Temperature, °C	k_1, min^{-1}	$k_2, \text{L mol}^{-1} \text{min}^{-1}$	$R^2, \text{first order}$	$R^2, \text{second order}$	$E_a, \text{kJ/mol}$
140	0.049	0.087	0.92	0.98	94.7
150	0.083	0.167	0.93	0.97	

Based on the second-order model data, the activation energy was determined to be 94.7 kJ/mol. This value was like those reported in other studies using heterogeneous catalysts. For example, Gao et al. (2025) obtained an activation energy of 93.84 kJ/mol using K_2CO_3 /activated carbon as catalyst.

This decrease is possibly due to catalyst deactivation caused by the reduction in the availability of active sites, which are affected by the presence of impurities such as free fatty acids (Mandari and Devari, 2022). This highlights the importance of exploring and implementing efficient washing processes to remove as many deposited impurities as possible during the reaction, thereby maximizing the number of available active sites (Burmana et al., 2024).

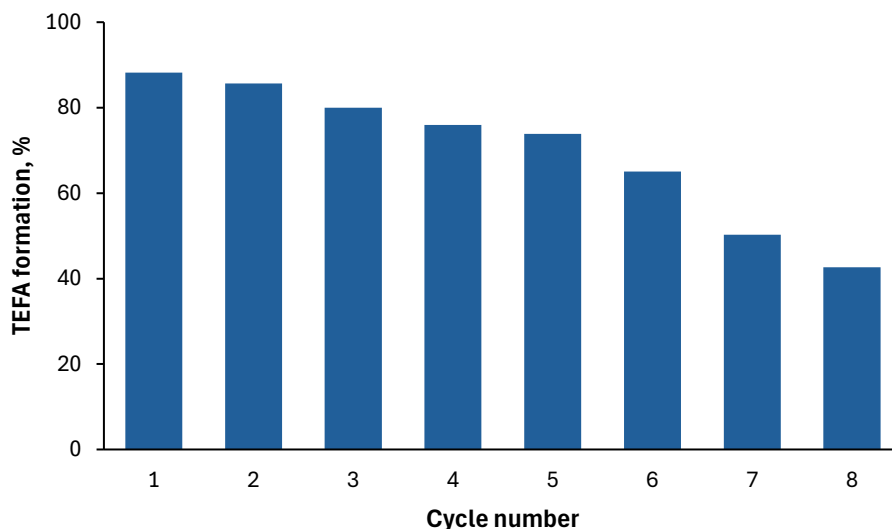


Figure 5.3 Reusability of the magnetic catalyst number 5

5.3.3 Physicochemical characterization of the catalysts

The physicochemical characterization by XRD confirmed the presence of magnetite in the catalyst used (see Figure 5.4). Both the unused catalyst and the one used in the final reaction cycle showed the characteristic peaks of magnetite located at 18.3, 30.2, 35.3, 37.0, 43.2, 53.5, and 57.3° (da Silva et al., 2023). However, these peaks were diminished after use. Meanwhile, the characteristic peaks of calcium hydroxide, the compound used to modify the material to confer catalytic properties, completely disappeared after use. The characteristic peaks of calcium hydroxide are located at 29.60, 34.11, 47.17, and 50.82°, as reported by Hossain et al. (2023). The decrease or complete absence of the characteristic peaks of the compounds present in the catalyst is possibly due, as previously mentioned, to the deposition of impurities that were not removed during the washing process (Burmana et al., 2024).

Additionally, the FTIR spectra (see Figure 5.5) confirmed the presence of magnetite in the catalyst through the characteristic Fe–O vibration band at 584 cm^{-1} (Chong et al., 2024), although with lower intensity than in the pure magnetite spectrum. However, this signal remains visible even after transesterification. Likewise, a band was identified around 3400 cm^{-1} , attributed to the stretching of the O–H group (Shao et al., 2024), possibly related to the use of cellulose acetate in the preparation of the material. On the other hand, in the catalyst spectrum, bands at 875 cm^{-1} are also distinguished, corresponding to the Ca–O bond, at 1054 cm^{-1} associated with the carbonate ion, and at 1415 and 1085 cm^{-1} , linked to the stretching of the C–O bond characteristic of calcium hydroxide (Cárdenas-Alvarado et al., 2025).

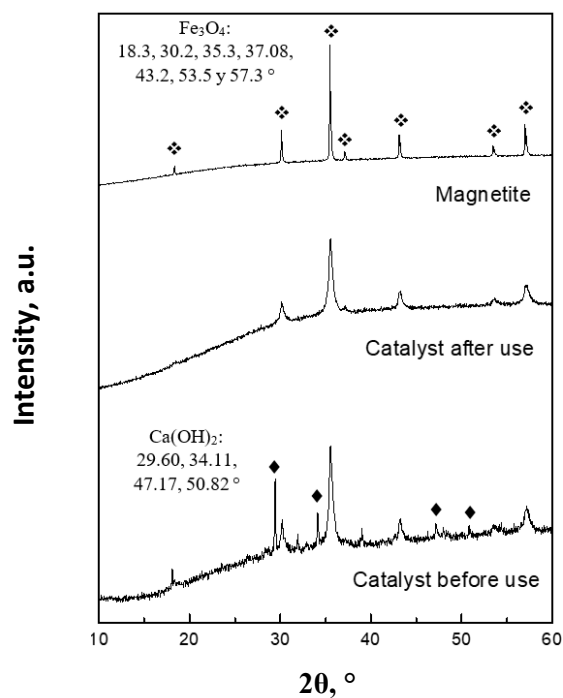


Figure 5.4 XRD diffractograms of magnetite, catalyst before and after use in transesterification of FAME

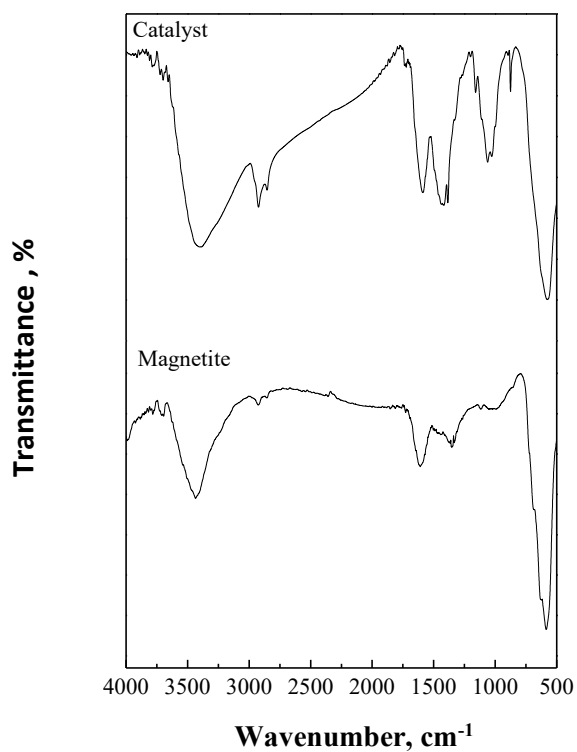


Figure 5.5 FTIR spectra of catalyst after use in transesterification of FAME and magnetite

5.4 Conclusions

The preparation of magnetic catalysts from cigarette filter waste modified with calcium hydroxide proved to be an effective and sustainable alternative for the synthesis of fatty acid trimethylolpropane esters, key compounds in biolubricant production. Through a factorial experimental design, the optimal synthesis conditions promoting the highest FATE formation were identified as 0.4 M calcium nitrate and 1 M sodium hydroxide. Additionally, the best transesterification conditions were determined, with 5 % catalyst usage and a biodiesel/TMP molar ratio of 1/1 being the most efficient, achieving a conversion of up to 91.83 %. Kinetic analysis revealed that the second-order model best fits the experimental data, with an activation energy of 94.7 kJ/mol, a value comparable to other heterogeneous catalysts. Although the catalyst showed good reusability for up to five cycles, its activity gradually decreased, attributed to the loss of active sites due to impurity deposition. Moreover, X-ray diffraction and FTIR spectra characterization confirmed the presence of magnetite and the disappearance of the calcium hydroxide phase after use, evidencing structural changes related to deactivation. These results highlight the potential of valorizing urban waste, such as cigarette butts, in the production of efficient and reusable catalysts for biolubricant synthesis.

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General conclusions

- Cigarette filter waste is a viable raw material for the synthesis of catalysts, transforming a waste with a high environmental impact into a functional material with energy applications.
- The incorporation of magnetite onto cellulose acetate fibers resulted in catalysts with greater catalytic efficiency compared to materials obtained through pyrolysis, achieving FAME yields of up to 99.5%.
- Functionalization with EDTA significantly improved the stability and durability of the catalysts, reducing the effects of magnetite oxidation and ensuring the preservation of catalytic and magnetic properties during extended storage periods.
- The modification with calcium hydroxide enabled the efficient production of FATEs, essential compounds in the synthesis of bio-lubricants, achieving conversions of more than 90%, thus confirming the potential of these materials for applications beyond biodiesel.
- The kinetic studies provided valuable information on reaction mechanisms, contributing to a better understanding of heterogeneous transesterification processes.
- A key advantage of the developed catalysts is their magnetic property, which allows for simple and rapid separation by applying a magnetic field, facilitating their recovery and reuse, with benefits in terms of sustainability and cost reduction.
- The physicochemical characterization of the catalysts and precursors was fundamental to understanding their composition, structure, and surface characteristics, which allowed the correlation of synthesis conditions with catalytic performance.
- The ability of catalysts to be reused in multiple cycles confirms their economic viability and potential for industrial applications.
- Together, this research demonstrates that it is possible to integrate waste valorization with the production of biofuels and biolubricants using magnetic heterogeneous catalysts, providing innovative and sustainable solutions to current energy and environmental challenges.

General recommendations

To complement the development of this project, it is recommended to:

- Determine the thermodynamic parameters of the transesterification reaction, as this information allows understanding the energetic aspects of the process to better describe the nature of the heterogeneous reaction. Among the thermodynamic parameters are Gibbs free energy, enthalpy, and entropy.
- Evaluate the reuse of catalysts through different regeneration methods, which is of great importance for reducing costs, increasing the sustainability of the process, and reducing the environmental impact associated with the production of new catalysts.
- Complement the physicochemical characterization of catalysts to fully understand their characteristics, properties, and composition, which will contribute to determining the effect of preparation and reaction variables on catalytic performance and to better explain transesterification.
- Evaluate different chelating and coating agents to identify those that improve magnetite preservation and prevent oxidation in catalysts, ensuring greater stability, durability, and efficiency in successive reaction cycles, as well as extending their shelf life.
- Evaluate the best-performing catalysts in the transesterification of waste oils or urban/industrial lipid sources, as this would not only contribute to reducing the cost of raw materials, but also promote waste valorization and the integration of circular economy schemes.

Blanca Paloma Escalera Velasco

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