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D.R.S.A.T.E.

POLITECNICO DI BARI

15

Doctor in Risk And Environmental, Territorial And
Building Development

2025

Coordinator: Prof. Vito Iacobellis

XXXVII CYCLE
CHEM-06/A

DICATECh

Department of Civil, Environmental,
Building Engineering and Chemistry

Maria Stella Leone

**Synthesis and upgrading of Waste Cooking Oil Bi-
odiesel using waste-based catalysts**

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Department of Civil, Environmental, Land, Building Engineering and
Chemistry
Polytechnic of Bari



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Rischio e Sviluppo Ambientale, Territoriale ed Edilizio

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Prof. Vito Iacobellis

CICLO XXXVII
CHIM-06/A

DICATECh
Dipartimento di Ingegneria Civile,
Ambientale, Edile e Chimica

Maria Stella Leone

**Sintesi e miglioramento del biodiesel ottenuto da
olio da cucina esausto utilizzando catalizzatori
derivati da rifiuti**

Prof.ssa Maria Michela Dell'Anna
DICATECh – Dipartimento di Ingegneria Civile, Ambientale,
Edile e Chimica
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EXTENDED ABSTRACT (eng)

This research work addresses the sustainable production of high-quality biodiesel from Waste Cooking Oil (WCO) through an innovative approach that integrates principles of circular economy and green chemistry. The work focuses on two main objectives: the first is the production of biodiesel via microwave-assisted transesterification using steel slag as a catalyst—a by-product of steel production—and the second is the improvement of biodiesel properties through partial hydrogenation reactions assisted by innovative nickel-based catalysts supported onto waste materials. The waste materials investigated for this purpose include steel slag and cellulose acetate derived from used cigarette filters, which were preliminarily subjected to a purification process using innovative and sustainable solvents, such as the deep eutectic solvents (DES). The proposed methodology aims to optimize the biodiesel production process by reducing energy costs while addressing environmental concerns associated with waste disposal. The results obtained demonstrated that the developed catalysts were efficient and selective, ensuring the production of biodiesel with oxidative stability and cold flow properties in accordance with the standards required by European regulations.

keywords

Waste cooking oil, biodiesel, transesterification, partial hydrogenation, steel slag, cellulose acetate, deep eutectic solvents, Nickel catalyst

EXTENDED ABSTRACT (ita)

Questo lavoro di ricerca affronta la produzione sostenibile di biodiesel di alta qualità partendo da oli esausti da cucina (Waste Cooking Oil, WCO) attraverso un approccio innovativo che integra principi di economia circolare e chimica verde. Il lavoro si concentra su due principali obiettivi, il primo è la produzione di biodiesel mediante transesterificazione assistita da microonde utilizzando scorie d'acciaio come catalizzatore, ovvero un sottoprodotto della produzione dell'acciaio e, successivamente, il miglioramento delle proprietà del biodiesel attraverso reazioni di idrogenazione parziale assistite da catalizzatori innovativi a base di nichel supportato su materiali di scarto. I materiali di scarto esaminati per questo scopo includono le scorie d'acciaio e l'acetato di cellulosa derivato dai filtri di sigarette usate, sottoposti preliminarmente ad un processo di purificazione mediante l'uso di solventi innovativi ed ecosostenibili, quali i solventi eutettici profondi (DES). La metodologia proposta mira ad ottimizzare il processo produttivo del biodiesel riducendo i costi energetici in concomitanza con le problematiche ambientali associate allo smaltimento dei rifiuti. I risultati ottenuti hanno mostrato che i catalizzatori sviluppati sono stati efficienti e selettivi, garantendo una produzione di biodiesel con valori di stabilità ossidativa e di proprietà di scorrimento a freddo conformi agli standard previsti dalla normativa europea.

keywords

Olio da cucina esausto, biodiesel, transesterificazione, idrogenazione parziale, scorie di acciaio, acetato di cellulosa, solventi eutettici profondi, catalizzatori di nichel

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CHAPTER I

GENERAL INTRODUCTION

1 GENERAL INTRODUCTION

1.1 Importance of biofuels

Greenhouse gas emissions (GHG) leading to global warming and consequently climate change are the most pressing and alarming environmental problems to be addressed in the current century. The combustion of fossil fuels is a major cause of climate change. Therefore, new sources of energy must be exploited to break the dependence on fossil and non-renewable sources. Biomass, or any organic material that comes from plants, trees, and agricultural and organic waste, is a very promising renewable source of energy and can lead to many kinds of valuable products, such as chemicals, biopolymers, biomaterials, and biofuels.¹ Biomass, firstly, is a renewable resource; secondly, it has formidable positive environmental properties, with zero net carbon dioxide (CO₂) emissions and very low sulphur content. Thirdly, it has significant economic potential, especially if fossil fuel prices increase in the future. Biofuels are liquid or gaseous fuels derived from biomass, their growing importance is related to the great advantages they offer, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply.² Biofuels can reduce the consumption of fossil fuels and therefore reduce carbon dioxide emissions, since they are considered carbon neutral since the carbon dioxide emitted when a biofuel is burned returns to the atmosphere from which it was captured through plants by means of photosynthesis. Therefore, biofuels appear to be a very effective means of reducing these emissions. The main types of biofuels include:

- **Bioethanol:** It derives from the fermentation process of sugars present in biomass (cellulose and hemicellulose). The biological process of fermentation occurs in anaerobic conditions by the action of microorganisms, usually yeast. Before fermentation into ethanol, cellulose must be hydrolyzed into glucose. Bioethanol can be produced from a large variety of

carbohydrates with a general formula of $(CH_2O)_n$. Bioethanol is used as an additive or substitute for gasoline.³

- **Biohydrogen:** obtained from biomass by steam reforming. All biomass materials can be converted to energy via a thermochemical process. Steam reforming is a chemical process used to produce hydrogen (H_2) and carbon monoxide (CO) from hydrocarbons, especially methane (CH_4) or natural gas, through a reaction with water vapor.⁴ Commercial catalysts are composed mainly of Transition elements such as iron and nickel that are both essentially plentiful and have an excellent performance.⁵ The further chemical reactions for most hydrocarbons that take place are $C_nH_m + nH_2O \rightarrow nCO + (m/2 + n)H_2$ with production of syngas.²
- **Biomethanol:** is a potential substitute for gasoline. It was used in the early last century to power cars, before cheap gasoline became widely available. Methanol is currently manufactured worldwide by conversion or derived from syngas, natural gas, refinery off-gas, coal or petroleum.⁶
- **Bio-oil:** It is a liquid fuel obtained from biomass (agricultural crops, municipal wastes and agricultural and forestry byproducts) via biochemical or thermochemical processes (pyrolysis).⁷ Bio-oil is a high-water content liquid mixture of various types of organic substances, including sugar monomers derived from cellulose/hemicellulose, sugar derivatives such as carboxylic acids, aldehydes, ketones, esters, alcohols and phenols derived from lignin.
- **Biodiesel:** is a mixture of methyl or ethyl esters of fatty acids produced from vegetable oils and animal fats through a transesterification reaction. Biodiesel represents a renewable and less polluting alternative to traditional diesel. In recent times, the use of vegetable oils, especially used vegetable oils for the production of biodiesel has acquired particular interest since this biofuel is less polluting and renewable than conventional diesel, which is a fossil fuel subject to depletion. The transesterification

reaction reduces the viscosity of the oil to make the final product suitable for the standard diesel engine.⁸

1.1.1 Biodiesel

Among the various fuels described, biodiesel is a very promising fuel that can replace conventional fossil fuels. Technically, it is a mixture of alkyl esters of fatty acids,⁹ produced through the transesterification of oils or fats in the presence of short-chain alcohols, such as methanol and ethanol, and a catalyst, giving glycerine as a by-product. It is an alternative diesel fuel, derived from renewable sources such as vegetable oils and animal fats. It is biodegradable, non-toxic and able of reducing engine emissions¹⁰ such as unburned hydrocarbons (-68% with respect to fossil fuels), particulate matter (-40%), carbon monoxide (-44), sulfur oxide (-100%), and polycyclic aromatic hydrocarbons (PAHs) (-80–90%). Meanwhile, it is safer to be stored and handled and can be easily produced in large quantities. Biodiesel is classified into four groups, called generations, depending on the nature of the feedstock.¹¹

- *First generation biodiesel*: prepared from edible oils deriving from agricultural materials such as cereals and sugar canes;
- *Second generation biodiesel*: deriving from non-edible oils of dedicated cultivars;
- *Third generation biodiesel*: deriving from waste vegetable oils;
- *Fourth generation biodiesels*: deriving from algae;

Sources for biodiesel production from vegetable oils are chosen based on the availability of raw materials in the country of production, which vary depending on the climate of the place and on the agriculture.¹² For example, in Canada mainly canola is produced,¹³ soybean in the United States of America (USA),¹⁴ palm oil in Malaysia,¹⁵ and *Jatropha curcas* in Nigeria¹⁶ while in European countries mainly rapeseed oil and corn oil are used.¹⁷ In terms of global production, Indonesia and the United States ranked as two of the largest producers of biodiesel in the world, with 7.9 and 6.5 billion liters produced in 2019 respectively.¹⁰ Although there is a global concern about

the employing of edible oils for biodiesel production, their use has been steadily increasing.¹⁸ Therefore, other non-edible oils like *Jatropha* oil, neem oil, castor oil and thallus oil are now exploited as alternatives in biodiesel production.¹⁹

From the point of view of environmental sustainability, using edible or non-edible vegetal oils as fuel feedstock is not recommended for the competition with the food chain or disadvantages regarding soil consuming.²⁰

Producing biodiesel from edible vegetable oils and non-edible oils of dedicated cultivars leads to competition for land between food production and biofuel production, resulting from both the growing demand for food and the growing global demand for energy for transportation. The consequences are deforestation and the conversion of pastures to cropland. These disastrous environmental effects are part of what is called 'indirect land use change' (ILUC). For this reason, it is of fundamental importance to preserve both food security and environmentally sustainable biofuel production by developing biodiesel from non-food resources. However, there are large quantities of low-cost oils and fats, such as restaurant waste and animal fats, that could be converted into biodiesel. Waste represents a precious resource for a sustainable future. In fact, the reuse of biological waste such as waste cooking oil (WCO)¹⁰ can lead to obtain a high-quality biodiesel, bringing the double advantage of avoiding competition with food chain and soil consuming, and at the same time it can solve the problems connected to waste disposal, thus promoting the principles of circular economy.²¹ Although the sale of automotives with internal combustion engine has been banned by the European Community starting from 2035, biodiesel still has many potentialities²² and its use will remain allowed for heavy-duty and long-distance transport, such as trucks and buses, which can continue to use it as an alternative to fossil fuels. European regulations stipulate that biodiesel can be blended with conventional diesel. Generally, the commercial blends are made of 7% of biodiesel (BD7). The blends are identified by a code that includes a number indicating the percentage of biodiesel content. Pure biodiesel, on the other hand, is designated with the code BD100.

1.1.2 Waste Cooking oil

Waste cooking oil (WCO) is an excellent feedstock for biodiesel production. Some estimates predict an annual production of 16.54 million tons (Mt) in major producing countries and regions such as China, Japan, North America, Europe, and Taiwan.²³ The increasing production of WCO is creating serious disposal issues. In most cases, WCO is discarded as waste and improperly disposed in garbage, soil or sewerage systems, leading to water treatment problems such as reduced sewer diameters and blockages in wastewater treatment plant infrastructure.²⁴ Therefore, appropriate management of WCO leads not only to environmental benefits, but also to economic advantages. The use of WCO as a raw material for biodiesel production makes the process very appealing from economic point of view, due to its low cost. The WCO price is two to three times cheaper than vegetable oils, and it also reduces the cost of waste product removal and treatment.²⁵ Indeed, the usage of waste edible oils can reduce biodiesel production costs by 60–90%.²⁶ The properties of waste cooking oil are different from fresh oil due to physical and chemical changes that occur during frying, such as oxidative and hydrolysis reactions. WCO has a higher content of Free Fatty Acids (FFA) and water than fresh oil. Although several techniques have been used to obtain biofuel from WCO, such as gasification or pyrolysis, the most widely used process is the catalytic transesterification of WCO in methanol to synthesize biodiesel, due to its economical and environmentally friendly procedure.²⁷ Free fatty acids (FFAs) pose a problem in the production of biodiesel from waste oils, because they react with commonly used alkaline catalysts (such as sodium or potassium hydroxide) to form soaps rather than the desired alkyl esters.²⁸ This side effect decreases the efficiency of the catalyst and reduces the biodiesel yield, making more difficult the separation of the final biodiesel from glycerine and other by-products due to an increase in viscosity and gel formation. The presence of water has a further negative effect as it triggers hydrolysis reactions in the triglycerides, further increasing the level of free fatty acids and promoting saponification during the process.²⁹ Therefore, usually the WCO should be first pre-treated or esterified with an acid catalyst before its transesterification reaction.²⁸

1.2 Aims and scope of the present thesis

This thesis is focused on the sustainable production of biodiesel using waste cooking oil (WCO) as feedstock. This approach is in line with the principles of circular economy, waste-to-value, and eco-sustainability, addressing important challenges such as pollution reduction, resource scarcity, and energy sustainability, issues that are becoming increasingly urgent in recent times. Converting waste materials into valuable biofuels helps reduce both the problems related to waste disposal and dependence on fossil fuels. This study initially turns its attention to the transesterification reaction of WCO, a well-established process for biodiesel production that is constituted of a mixture of fatty acid methyl esters (FAMES). The use of steel slag, a by-product of steel processing, as a novel catalyst in the transesterification reaction is investigated. In this case, the transesterification reaction is performed using microwave irradiation to reduce energy consumption compared to traditional heating methods. Using waste materials brings economic and environmental benefits. Therefore, in this study, both the feedstock (WCO) and catalysts come from waste resources. Following the transesterification process and subsequent biodiesel production, this thesis focuses on upgrading the properties of biodiesel through partial hydrogenation reactions. This step improves the oxidative stability of the fuel and its overall performance. The hydrogenation reaction requires the use of catalysts to aid the process. The study is focused on the synthesis of innovative nickel-based catalysts supported onto waste materials such as steel slag and cellulose acetate derived from used cigarette filters. Their catalytic activity is then investigated. Therefore, this thesis is structured into three main chapters.

The first chapter focuses on the microwave-assisted transesterification reaction employing steel slag as a catalyst. The second chapter explores the synthesis and application of nickel-based catalysts supported onto steel slag for the improvement of biodiesel properties. Finally, the third chapter delves into the synthesis of nickel catalysts supported onto cellulose acetate extracted from cigarette butts. The

purification of cellulose acetate performed by employing Deep Eutectic Solvents (DES), an innovative and environmentally friendly extraction technique described in the thesis, will be explored initially. The use of DESs provides a sustainable alternative to traditional organic solvents, such as acetone or chloroform, due to their low toxicity, biodegradability and reduced volatility. These characteristics make them ideal tools for promoting greener and more efficient chemistry in industrial processes. By integrating waste valorization strategies at all stages of biodiesel production and upgrading, this thesis aims at demonstrating the possibility of sustainable biofuel production, with both positive environmental and economic repercussions. The knowledge gained through this study represents a contribution to the development of green chemistry and solutions based on circular economy principles.

CHAPTER II

MICROWAVE ASSISTED BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING STEEL SLAGS AS CATALYST

2 MICROWAVE ASSISTED BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING STEEL SLAGS AS CATALYST

2.1 Introduction

In this research work, an innovative catalytic system was designed for the synthesis of biodiesel starting from waste biomass (waste cooking oil, WCO) using waste material (steel slags) as a catalyst under microwave irradiation. This procedure comprised the use of unmodified waste steel slags as alkaline catalyst under microwave irradiation to lower energy consumption with respect to conventional heating. To the best of our knowledge, the microwave-assisted transesterification of WCO catalyzed by unmodified steel slags has never been reported to date. In fact, steel slags without any modification have been successfully employed as catalyst for the preparation of biodiesel under conventional heating using soybean oil as the feedstock,³⁰ while doped waste steel slags have been used for the transesterification of palm oil.³¹ However, in the presence of neat steel slags long reaction time (12 h) and high tem-

peratures (120 °C) have been required to reach reaction completion, with edible oils being used as starting feedstock,¹⁵ making the whole process economically inconvenient. Indeed, it is world-wide recognized that microwave irradiation ensures a more efficient and faster heating than conventional methods, enabling a considerable energy saving. In fact, the microwave assisted synthesis of biodiesel has been already developed using papaya oil as the feedstock in the presence of sodium hydroxide.³² On these bases and aiming at developing a sustainable procedure for the synthesis of biodiesel from WCO, herein a microwave-assisted transesterification of WCO with unmodified steel slags is described, employing the Design of Experiment (DoE) to assess the simultaneous evaluation of the parameters (reaction time, temperature, weight of catalyst)³³ that could affect the final yield.

2.1.1 Transesterification reaction

There are various methods for producing biodiesel from WCO, including supercritical methods,³⁴ gasification or pyrolysis,²³ but transesterification is considered the most favourable for biodiesel production,¹⁰ due to its cost-effective.

Transesterification converts the triglycerides present in oil into alkyl esters of fatty acids (biodiesel), generating glycerine as a byproduct.³⁵ This process, also known as alcoholysis, commonly uses alcohols such as methanol, ethanol, propanol, butanol, and amyl alcohol.³⁶ (**Figure 1**)

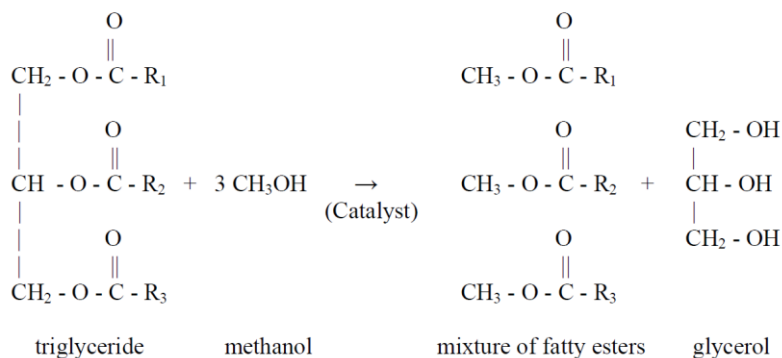


Fig. 1 - Transesterification of triglycerides in methanol

During the reaction, three molecules of alkyl esters are produced for every molecule of glycerol (Figure 1). Transesterification is employed to reduce the viscosity of vegetable oils, lower their molecular weight, and improve their volatility. It is preferred over the direct esterification of fatty acids since triglycerides are more readily available and abundant. This process allows for the production of pure biodiesel (B100), which, after an upgrading process, can be blended with fossil diesel in various proportions.

The parameters influencing the reaction include temperature, time, pressure, alcohol-to-oil ratio, type of catalyst, mixing intensity, and the nature of the starting oil. The reaction is promoted by acid or alkaline catalysts under homogeneous^{37,38} or heterogeneous conditions.³⁹ The homogeneous catalytic systems often use sulfuric acid or potassium hydroxide, that are relatively expensive and cause the formation of a great amount of strong acidic or basic wastes.⁴⁰ The transesterification of triglycerides catalyzed by alkalis is fast and allows high conversions to be achieved easily at temperatures between 40 and 65 °C. Furthermore, alkaline catalysts are less corrosive than acidic compounds. Acids catalyze the esterification of free fatty acids to produce fatty acid esters, increasing biodiesel yield and preventing the saponification reaction. However, acid-catalyzed transesterification is much slower than alkali-catalyzed reactions and also requires more extreme temperature and pressure conditions. For all these reasons, in industrial applications, alkaline catalysts such as sodi-

um or potassium hydroxide are preferred to acidic catalysts. To overcome the disadvantages related to the use of homogeneous catalysts (such as waste disposal, use of expensive catalysts and so on), the employing of recyclable heterogeneous catalysts has become appealing in the recent years and many studies have been devoted to the development of heterogeneous catalytic systems that could be recycled several times.^{22,39} Recently, both the academic and industrial communities have dedicated growing attention in developing new catalysts able to improve the efficiency of the biodiesel production, reducing the disadvantages associated with traditional catalysts and promoting more sustainable solutions. Among them, it has been reported the use of catalytic materials obtained from waste. Some examples are listed in table 1. Mollusk shells, such as those of crabs,⁴¹ oysters,⁴² sea snails,⁴³ and freshwater mussels,⁴⁴ have been successfully used as sources of calcium oxide. The calcined shells of these mollusks have demonstrated high efficiency in transesterification, achieving biodiesel conversion rates close to or exceeding 90%, often within a few hours of reaction time. Similarly, chicken⁴⁵ and quail⁴⁶ eggshells have proven to be an excellent source of CaO, ensuring biodiesel yields above 95%. However, in the presence of atmospheric carbon dioxide and water, the active sites of CaO become poisoned, making the catalyst ineffective and insensitive to raw materials with a free fatty acid (FFA) content greater than 2%.⁴⁷

Ashes, particularly those derived from the combustion of empty palm fruit bunches⁴⁸ (Empty fruit bunch ash, EFBA) and fly ash⁴⁹ produced from coal combustion processes, have also been applied as catalysts. Palm fiber-based ashes mainly contain potassium oxide, silica, and calcium oxide, which enable efficient transesterification, achieving conversions above 90% in less than an hour. However, their sensitivity to moisture and free fatty acids limits their applicability. Fly ash, an inorganic waste generated from coal combustion processes, typically constituted of approximately 55% SiO₂, 30% Al₂O₃, and other oxides, has been used as a support for CaO, improving the stability and reusability of the catalyst. However, some studies have shown that the leaching of active components reduces efficiency in subsequent cycles.⁵⁰

Rocks such as alum,⁵¹ dolomite,⁵² and calcite⁵³ represent another alternative for catalysis in biodiesel production. Alum has shown high conversion efficiency for palm oil but requires a high methanol-to-oil molar ratio and a long reaction time. Finally, animal bones have also been used as catalysts for biodiesel synthesis. Calcined Rohu fish⁵⁴ or sheep bones⁵⁵ have exhibited a high methyl ester conversion rate (97.73%) and stability for up to six reuse cycles.

Depending on the specific case, these catalysts require a preparation process that includes calcination at temperatures ranging from 800°C to 1000°C for several hours.

In this overview, another catalyst which has been found extremely promising for biodiesel synthesis, is steel slag, due to its high content of basic metal oxides.⁴⁰ Steel slags can be divided into by-products and waste⁵⁶ and they can be used in their raw form without any modifications.

Table 1: Selected examples of catalytic materials obtained from waste used for biodiesel production.

Waste source	Catalyst	Optimum reaction conditions	FAMES yield	Sustainability	Disadvantages
<i>Mollusc shells (Freshwater mussel)</i>	CaO	$T = 70\text{ }^{\circ}\text{C}$, $t = 1,5\text{ h}$ MeOH/oil = 12:1 Catalyst (wt%) = 5%	>96%	Low cost, derived from waste, high basicity	Sensitive to moisture and carbon dioxide, requires calcination before use
<i>Egg shells</i>	CaO	$T = 60\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$ MeOH/oil = 12:1 Catalyst (wt%) = 10%	95%	Low cost, derived from waste, high basicity	Sensitive to moisture and carbon dioxide, requires calcination before use
<i>Ashes (EFBA)</i>	K_2O	$T = 60\text{ }^{\circ}\text{C}$, $t = 0,5\text{ h}$ MeOH/oil = 15:1 Catalyst (wt%) = 3%	90%	Low cost	Moisture intolerance
Coal fly ash loaded KNO_3	K_2O	$T = 70\text{ }^{\circ}\text{C}$, $t = 8\text{ h}$ MeOH/oil = 15:1 Catalyst (wt%) = 15%	87%	Cheap, plentiful	Leaching of active compounds
Dolomite	$CaMg(CO_3)_2$	$T = 60\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$	98%	Good thermal	high methanol/oil

		<i>MeOH/Oil=30:1</i> <i>Catalyst (wt%) = 6%</i>		stability, plentiful	ratio
Alum	$KAl(SO_4)_2$	<i>T = 170 °C, t = 12 h, MeOH/oil = 18:1</i> <i>Catalyst (wt%) = 7%</i>	93%	Good thermal stability, plentiful	Requires high reaction temperatures for high reaction times
Sheep bone	Hydroxyapatite	<i>T= 65°C, t=4h, MeOH/oil = 18:1</i> <i>Catalyst (wt%) = 20%</i>	97%	Low cost	Sensitive to moisture and carbon dioxide, requires calcination before use

2.1.2 Steel Slags

Steel slag is a solid by-product generated from steel production (Figure 2).



Fig. 2 – Steel slag, residual byproduct from the steelmaking process

It represents the primary solid waste produced during the steel manufacturing process, accounting for 15–20% of the total output. In 2021, steel slag production in China alone exceeded 120 million tons.⁵⁷ Most steel slags cannot be utilized immediately and are either buried or stored outdoors, occupying a significant amount of land and causing soil and groundwater pollution. Furthermore, steel slag contains various components, including heavy metals, which can leach into soil and water, posing threats to ecological systems and human health.

Additionally, if steel slag is mismanaged during treatment and transportation, large amounts of dust can be generated, leading to environmental pollution and health

risks. For this reason, it is essential to revalorize this waste, shifting from a linear to a circular development model. This approach is a winning strategy that simultaneously prevents resource depletion and waste accumulation.

The iron and steel manufacturing industries produce four types of slags, named according to the processes in which they are generated: Blast Furnace Slag (BFS), Basic-Oxygen Furnace Slag (BOFS), Electric-Arc Furnace Slag (EAFS), and Ladle Furnace Slag (LFS) (Figure 3)

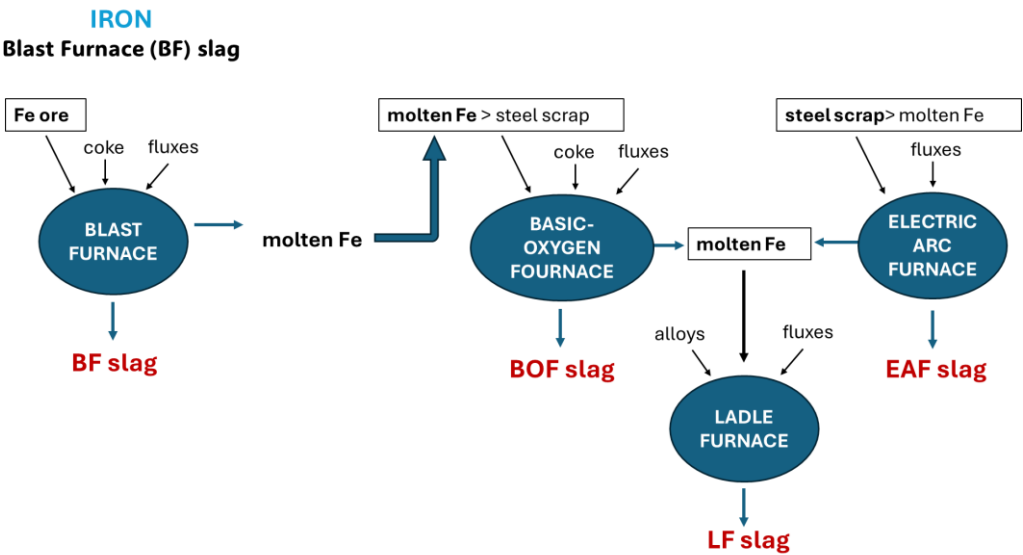


Fig. 3 - Types of steel slag generated in iron and steel manufacturing processes, including Blast Furnace Slag (BFS), Basic-Oxygen Furnace Slag (BOFS), Electric-Arc Furnace Slag (EAFS), and Ladle Furnace Slag (LFS).

BFS is formed during the production of liquid iron, which is the first step in making steel. It is created at a high temperature (about 1600°C) in a blast furnace when iron ore (or iron oxides) is reduced to molten iron, with coke used as fuel and limestone added as a fluxing agent.

At the end of the process, BFS can be quickly cooled using large amounts of high-pressure water to form water-cooled slag or slowly cooled in air to form air-cooled slag. These two different cooling methods create BFS with different physical and chemical properties.⁵⁸ Steel slag is produced when molten iron from the blast

furnace and steel scrap are combined with alloys to create a specific type or grade of steel. The primary types of steel slag are usually categorized based on the type of furnace used: basic oxygen furnace (BOF) and electric arc furnace (EAF).

A BOF uses large amounts of oxygen to oxidize the charge, which primarily consists of molten iron with smaller amounts of steel scrap. Large volumes of molten iron from the blast furnace are combined with steel scrap in the steelmaking vessel and reacted with oxygen.⁵⁹ Lime and dolomite are added to form slag and remove impurities. At the end of the reaction, the steel and slag are separated, and the slag is poured into ground bays to be cooled with water sprays.⁴⁴

An EAF, on the other hand, uses an electric current to generate the heat required to melt recycled steel scrap, with smaller amounts of molten iron from the blast furnace. Temperatures in these furnaces fluctuate but commonly reach about 1650°C.⁶⁰ An EAF is considered the primary stage of the steel purification process, during which steel scrap is transformed into molten steel. EAF slag (EAFS) and molten steel are the final products of this process. The EAFS is discarded, and the molten steel is transferred to the ladle furnace for secondary purification.⁶¹

Steel slag is typically cooled slowly under atmospheric conditions, forming crystalline materials. In addition to slag produced during the primary steelmaking stage, slag is also generated during secondary steel refining operations that adjust carbon content and remove sulfur, gases, or other impurities. Molten iron from the BOF and EAF processes can be refined in a ladle furnace with the possible addition of alloys and flux materials to produce different grades of steel. The slag produced in this process is called ladle furnace slag (LFS).

Steel furnace slags are cooled similarly to iron slags, and they have comparable properties, and are used for similar purposes. The construction sector represents the largest application for steel slag recovery. In Europe, the amount of steel slag produced in 2010 was approximately 21.8 million tons.⁶² A significant portion of this slag is reused and recycled, mainly in road construction. However, secondary metallurgical slags have a low recycling potential, due to their highly variable mineralogical composition. Furthermore, they contain high levels of CaO and MgO in different pro-

portion due to several factors, such as the variety of metallurgical processes, batch synthesis, and variations in scrap metal.⁶³

Moreover, the handling of slag in slag storage sites must also be considered. This means that the potential reuse of each type of secondary steel slag must be assessed individually on a case-by-case basis.

2.2 Characterization of Steel Slags

Steel slags (SS) employed in the present study derived from the secondary slag of the steel making factor “Acciaierie d'Italia” placed in Taranto (Italy). The SS used in this work are wastes, they were produced in the time range 1972–1980 and left in an open-air disposal site for more than 40 years, before being removed due to environmental contamination concerns. By reusing this aged slag, this approach not only mitigates the long-term environmental impact of steelmaking waste, but also contributes to more sustainable steelmaking waste management, potentially reducing the overall carbon footprint of the whole process. The SS used in this work were sieved below 80 mesh (177 μm) before use. (Figure 4)



Fig. 4 - SS sieved below 80 mesh (177 μm) before use

The steel slags were characterized using SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray Spectroscopy), XRF (X-ray Fluorescence), FT-IR (Fourier Transform Infrared Spectroscopy), and TGA-DSC (Thermogravimetric Analysis coupled with Differential Scanning Calorimetry).

SEM image of the sieved SS (Figure 5) revealed a polydisperse sample made of particles and granules of different sizes. EDX mapping (Figure 6) showed a related

homogeneous elemental distribution of Ca, Al and Na together with O. On the contrary, the mutually related distribution of Mn, Mg and Fe was quite uneven, being their concentration higher in some regions with respect to others. Si also showed an uneven distribution, being related to oxygen distribution. Traces of chloride, phosphorus and sulphur were also detected by EDX analysis.

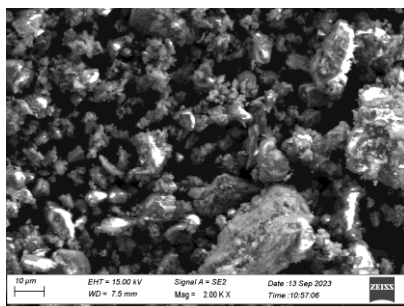


Fig. 5 – SEM micrograph of the investigated steel slags

EDX (Na, Mg, Al) and XRF (Si, Ca, Mn, Fe, Ti) elemental analyses (Table 2) showed that Ca is the most abundant element (31.2 %), followed by Fe (18.8 %), Mn (4.7%) and Si (3.8 %). Na, Mg and Al content was roughly estimated by EDX analysis as less than 3%.

Table 2. Elemental analysis of the investigated steel slags carried out by EDX and XRF analysis.

Element	Weight % (SEM/EDX)	Weight % (XRF)
Si		3.8 ± 0.2
Ca		31.2 ± 1.8
Mn		4.7 ± 0.4
Fe		18.8 ± 1.4
Na	0.7 ± 0.2	
Mg	0.8 ± 0.2	
Al	0.5 ± 0.2	

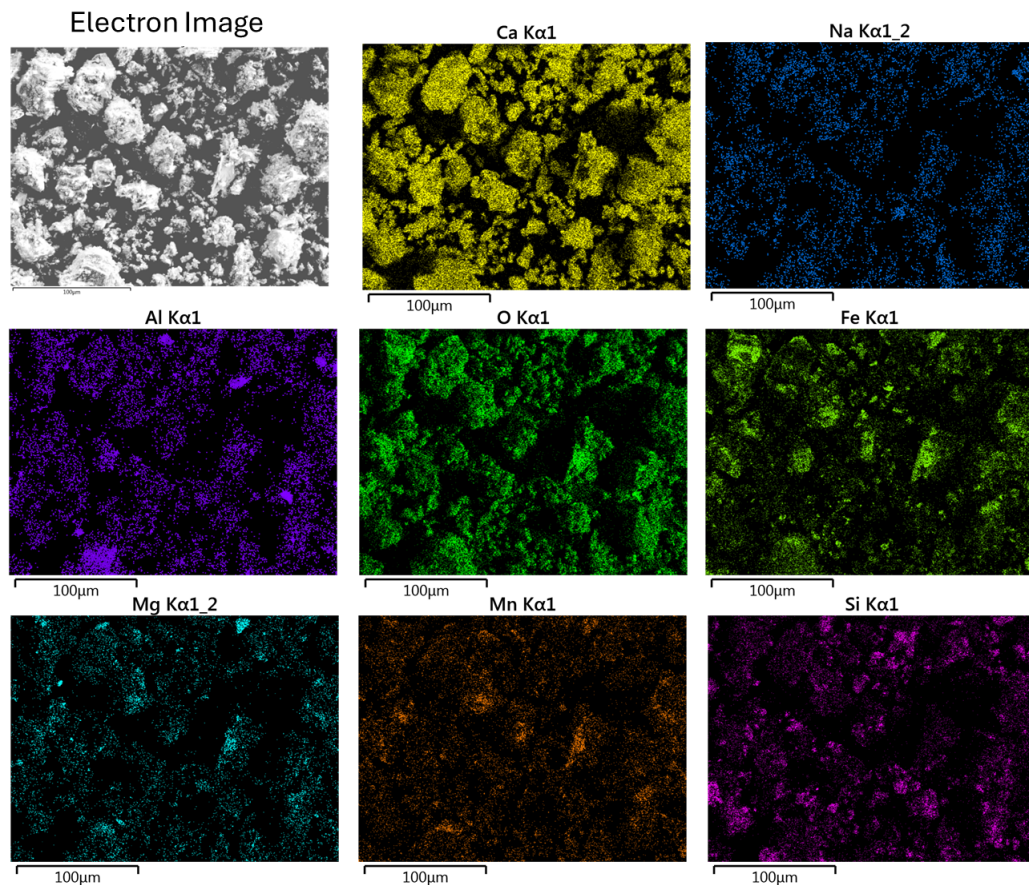


Fig. 6 - SEM/EDX mapping of the investigated steel slags

XRD analyses of SS (Figure 7) revealed the presence of portlandite (Ca(OH)_2 , CS: 42.4 nm), calcite (CaCO_3 , CS: 42.4 nm), quartz (SiO_2 , CS: 757,0 nm), brownmillerite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$, CS:73.0 nm), dolomite ($\text{CaMg(CO}_3)_2$, CS: 42.4 nm), larnite (Ca_2SiO_4 , 89.2 nm) and hematite ($\alpha\text{-Fe}_2\text{O}_3$, CS: 42.4 nm), along with a significant amount of amorphous compounds, as suggested by the low level of signal/noise ratio in the diffractogram. The obtained results are consistent with the known nature of SS, made up of an ensemble of metal oxides (mainly CaO), hydroxides, aluminates, silicates and carbonates.

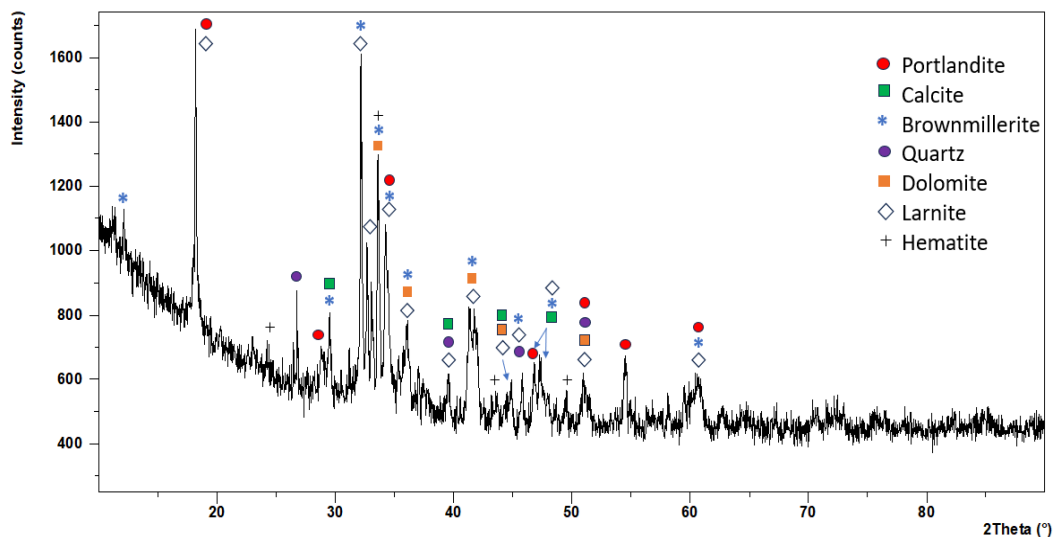


Fig. 7 – XRD diffractogram of the investigated steel slags.

SS were also subjected to TGA/DSC analyses and the related thermogravimetric curves (Figure 7) displayed the endothermic transformations (Figure 7a) and the decomposition temperatures (Figure 7b) of the compounds detected by XRD.

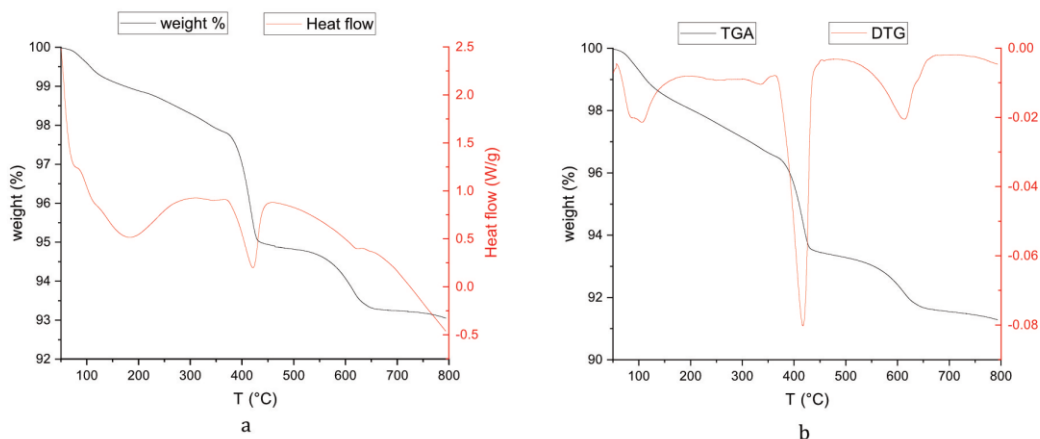


Fig. 8 - (a) TGA/DSC and (b) TGA/DTG (DTG=derivative TG) curves of SS. The main weight losses are at 100 °C (water), 416 °C (portlandite dehydroxylation), 619 °C (magnesite decarbonatation).

A constant weight loss observed between 50 and 600°C could be ascribed to the loss of intralayer water and dehydration of calcium silicates.^{64,65} Meanwhile, the two detected major weight losses could be related to the endothermic dihydroxylation of portlandite to calcium oxide and water at about 460°C⁶⁴ and to the decarbonation of magnesium carbonate at about 620°C,⁶⁶ respectively. Also, an incipient weight loss appears at around 800°C that could be ascribed to the decarbonation of calcium carbonate and/or dolomite.^{64,67}

ATR-FT-IR spectra were recorded on steel slags before and after TGA analysis (Figure 9).

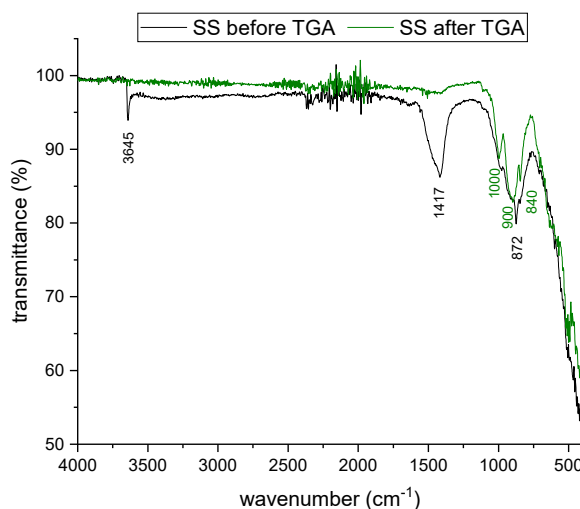


Fig. 9 – ATR-FT spectra of the investigated steel slags before (black curve) and after TGA analysis (green curve)

Three main bands could be identified in the spectrum of pristine SS (Figure 9, black curve). The first band at 3645 cm^{-1} is a characteristic signal ascribable to the stretching of the O-H group in Ca(OH)_2 and its low intensity and small peak width indicate the absence of hydrogen bond formation.⁶⁸ The second band at 1417 cm^{-1} can be ascribed to the stretching of the C-O bond,^{68,69,70} while the third band is an overlapping of many signals, in which it could be recognized the one at 872 cm^{-1} ,

tentatively assigned to Ca- O bending.⁶⁸ However, in the same region lie also the absorption peaks due to out-of-plane bending vibration modes of carbonate ion (CO_3^{2-})⁷¹ and Si- O- Si bonds,^{68,69} both contributing to the observed IR band. Regarding the spectrum of SS recovered after TGA analysis (Figure 9, green curve), the bands related to O- H and C- O stretching detected in the spectrum of pristine SS (Figure 9, black curve) are no longer present and only three peaks are visible, all of them falling between 1000 and 840 cm^{-1} , typical for the presence of metal oxides, deriving from the thermal decomposition of hydroxides and carbonates during TGA analyses.

2.3 Transesterification reaction using SS as catalyst

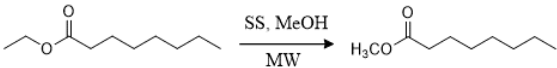
The investigated SS showed high basicity (due to the presence of metal hydroxides, oxides, and carbonates) which makes them a promising heterogeneous catalyst for the transesterification reaction.⁷² In fact, after mixing SS with deionized water in 1 : 2.5 mass ratio, the water phase suddenly reached the pH value of 12.0. Transesterification experiments were carried out in an ETHOS ETOUCH Milestone microwave applicator

2.3.1 Transesterification of Ethyl Octanoate

Before evaluating steel slags as active catalysts for the microwave-assisted transesterification reaction of waste cooking oil (WCO), an optimization process for the catalytic system has been undertaken by focusing on the transesterification of ethyl octanoate into methyl octanoate, which served as a benchmark reaction. This model reaction was selected for its simplicity and practicality during workup procedures. Unlike the more intricate catalytic system involving WCO as the substrate and fatty acid methyl esters (FAMES) as the products, this reaction offered a more straightforward approach to monitoring the catalytic performance and reaction progress. Such an approach ensures precise evaluation of the catalytic system under controlled conditions, before applying the catalyst to more complex reactions involving real-world substrates like WCO. Transesterification reactions were carried

out in a 25 mL PTFE vessel tube containing 0.50 mmol of ethyl octanoate in 12 mL of CH₃OH in the presence of the proper amount of catalyst. Microwave irradiation was used up to 500 W, the temperature being ramped from room temperature to the required temperature in 1.5 minutes and the sample being held under stirring at this temperature for the desired time. The results obtained in the benchmark reaction was monitored by GLC and are summarized in Table 3, showing that 300 mg catalyst and 10 min reaction are sufficient to warrant very good conversion (93 %, entry 3, Table 3). Conversions as high as 98% were achieved in the presence of 400 mg of SS at 130°C with a reaction time of 30 min (entry 6, Table 3) or at 150°C for 20 min (entry 8, Table 3). Conversion and selectivity were assessed by GLC analyses.

Table 3. Transesterification reactions of ethyl octanoate (benchmark reaction)

				
Entry	Amount of SS (mg)	T (°C)	t (min)	Conv. (%)
1	200	130	10	64
2	250	130	10	85
3	300	130	10	93
4	300	130	15	94
5	400	130	10	93
6	400	130	30	98
7	500	130	20	94
8	400	150	20	98
Reaction conditions: 0.50 mmol of ethyl octanoate, 12 mL of CH ₃ OH and SS were stirred under MW irradiation for the desired time at the required				

2.3.2 Transesterification of WCO

Once the optimal reaction conditions for the model substrate were identified, the focus shifted to studying the transesterification of WCO. In this case, transesterification reactions were carried out in a 25 mL PTFE vessel tube by adding 10 mL of CH₃OH to 922.1 mg (1.0 mL) of WCO in the presence of 400 mg of SS as

catalyst. The WCO/CH₃OH volume ratio equal to 10 was set based on literature data.^{31,32,38} Microwave irradiation was used up to 500 W, the temperature being ramped from room temperature to the required temperature in 1.5 min and the sample being held at this temperature under stirring for the desired time. After cooling down to room temperature, the reaction mixture was centrifuged (4000 rpm, 15 min), and the liquid methanol phase was pipetted into a separating funnel, leaving the solid and any unreacted WCO (insoluble in methanol) in the centrifugation tube for further purification.

Afterwards, 20 mL of *n*-heptane and 10 mL of aqueous saturated NaCl solution were added to the methanol solution in the separating funnel. After being removed from the organic phase, the aqueous phase was washed with *n*-heptane (2×20 mL) and the organic phases were collected and dehydrated with sodium sulphate. Once filtrated, the obtained solution was placed in a (previously weighted) crystallizer and let overnight under a fumehood to evaporate the solvent. The weight of FAMES (*w*FAMES) was measured, and the yield was assessed as:

$$yield = \frac{w_{FAMES}}{w_{WCO}} \cdot 100$$

Equation 1

where *w*_{WCO} is the weight of the used WCO.

The catalyst and the unreacted WCO, removed of the methanol phase after reaction (as described in the previous paragraph) were added of 5 mL of acetone already used to wash the employed reaction PTFE vessel. The obtained mixture was centrifuged (4000 rpm, 15 min) and the acetone solution was placed in a (previously weighted) crystallizer and let overnight under the fume hood to evaporate the solvent. The unreacted WCO was weighted, and the conversion was assessed as:

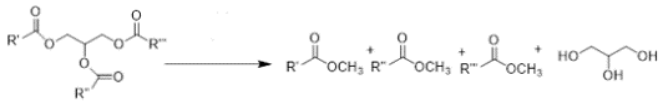
$$conv = \frac{w_{WCO} - w_{NRWCO}}{w_{WCO}} \cdot 100$$

Equation 2

Where *w*_{WCO} is the weight of the used WCO and *w*_{NRWCO} is the weight of the unreacted WCO. The recovered catalyst was added of acetone (5 mL) and sonicated

for 15 min. The mixture was then centrifuged (4000 rpm, 15 min) and the upper phase discharged. Methanol (5 mL) was then added to the solid catalyst and the resulting mixture was sonicated for 30 min. The catalyst was filtered off and dried in an oven at 80°C overnight for subsequent catalytic runs. All tests were performed in three replicates, obtaining comparable results. The transesterification reactions were carried out by varying both the temperature and the reaction time. The obtained results are collected in Table 4.

Table 4. Transesterification reactions of WCO to FAMES

			
Entry	T (°C)	T (min)	Conv. (%)
1	130	30	>95
2	120	30	>95
3	110	20	>95 ^[a]
4	90	20	68
Reaction conditions: 1.0 mL (922 mg) of WCO, 10 mL of CH ₃ OH and SS (400 mg) were stirred under MW irradiation for the desired time at the required temperature. [a]: The isolated yield of pure FAMES, assessed as described in the Experimental Section, was 85%.			

By carrying out the catalytic test at T=130°C and t=30 min, the conversion of WCO was >95% (entry 1, Table 4). The MW-assisted transesterification of WCO gave conversion >95% also at T=120°C and reaction time of 30 min (entry 2, Table 4) and at T=110°C and reaction time of 20 min (entry 3, Table 4). The conversion was significantly lower when the reaction was carried out at 90°C (entry 4, Table 4).

2.4 Design of Experiment (DoE)

Data shown in Table 4 prompted us to apply the DoE to gain insights into the possible interactions among variables affecting the reaction course and to pinpoint the optimal conditions for the MW-assisted transesterification of WCO. The reported studies of DoE applied to biodiesel synthesis^{30,32,73} have considered as main variables the substrate/solvent ratio, the catalyst weight, the reaction time, and the temperature. In the present work, the substrate/solvent ratio was set to 1 : 10, because it has been widely recognized as the best ratio for achieving the highest oil conversion.^{31,32,38} The other variables (catalyst weight, reaction time, and temperature) were used as factors.

The range values were set as follows: $T=80\div140^{\circ}\text{C}$, $\text{time}=15\div45\text{ min}$, $\text{catalyst weight}=200\div400\text{ mg}$. Different type of design can be chosen for the optimization process. In this work Box-Behnken Design (BBD) was selected because when three factors are taken as input parameters (as in the present study) BBD performs better (and requires fewer runs) with respect to the alternative Central Composite Design (CCD). Moreover, aiming at maintaining the rotability of the design (the design could be rotated around its center point without changing the prediction of variance), center points were added.⁷⁴ The experiments carried out following the Box-Behnken design are shown in Figure 10.

	Exp No	Exp Name	Run Order	Incl/Excl	Temperature	time	catalyst weight	conversion
1	1	N1	4	Incl	80	15	300	18.16
2	2	N2	9	Incl	140	15	300	96.6
3	3	N3	15	Incl	80	45	300	31.6
4	4	N4	10	Incl	140	45	300	96.98
5	5	N5	1	Incl	80	30	200	16.3
6	6	N6	2	Incl	140	30	200	96.3
7	7	N7	11	Incl	80	30	400	38.98
8	8	N8	14	Incl	140	30	400	96.72
9	9	N9	5	Incl	110	15	200	27.3
10	10	N10	7	Incl	110	45	200	56.26
11	11	N11	12	Incl	110	15	400	87.06
12	12	N12	13	Incl	110	45	400	95.85
13	13	N13	6	Incl	110	30	300	73.69
14	14	N14	8	Incl	110	30	300	74.53
15	15	N15	3	Incl	110	30	300	74.08

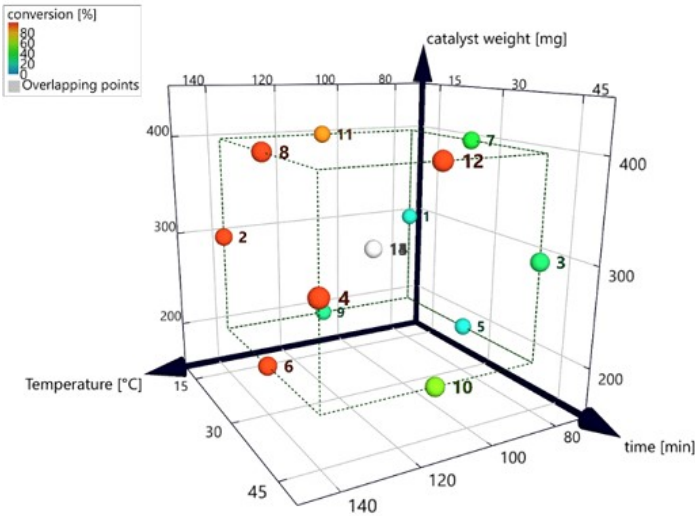


Fig. 10 - Visual representation of the BBD experiments

The multiple regression coefficients of the model obtained with the software MODDE 13 are collected in Table 5. The significance of each coefficient was established by the p -value (probability <0.05). Quadratic and interaction coefficients, as well as the linear coefficient of “reaction time” resulted not significant (p -value >0.05) (red values in Table 5). On the contrary, the linear coefficients of “temperature” and “catalyst weight” resulted significant, at a confidential level of 95%. This statistical output suggests that there is no correlation between the three chosen varia-

bles, which therefore affect independently the system. Moreover, the variables influence the WCO conversion with a linear (not quadratic) correlation. Furthermore, in the range investigated, ‘reaction time’ does not impact the system, and only “catalyst weight” and “temperature” affect the reaction conversion.

Based on these statistical considerations, the model was modified, and all non-significant coefficients (together with associated variables) were removed. The final model is described by the following equation, where A and C refer to “temperature” and “catalyst weight”, respectively:

$$conv = \beta_0 + \beta_1 x_1 + \beta_3 x_3 = 65 + 35A + 15C \quad \text{Equation 3}$$

To determine the fitness and significance of the regression model, analysis of variance (ANOVA) was carried out, and the relevant results are reported in Table 6. The model fits properly the data, with a R^2 of 0.870 and a p -value associated to the regression equal to zero, indicating the adequacy of the predicted model. On the other hand, the p -value lower than 0.05 associated to the lack of fit does not indicate that there is a lack of fit in the model. In fact, in this case the high reproducibility obtained for the centered points of the DoE caused an extremely low pure error with the artefact of obtaining a very high F -test value, which in turn led to a low p -value.⁷⁵

Table 5. Regression coefficients estimation for WCO conversion

Coefficient	Coeff. value	Std. Err.	P-value ^[a]	Conf. int
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Constant (β_0)	74.1	7.31807	0.000161009	18.8117
Linear				
β_1 (A: temperature)	35.195	4.48138	0.00053744	11.5198
β_2 (B: reaction time)	6.44625	4.48138	0.209829	11.5198
β_3 (C: catalyst weight)	15.3062	4.48139	0.0189299	11.5198
Square				
β_{11} (A^2)	-8.90376	6.59642	0.234973	16.9567
β_{22} (B^2)	-4.36125	6.59642	0.537757	16.9567
β_{33} (C^2)	-3.12125	6.59642	0.656027	16.9567
Interaction				
β_{12} (AB)	-3.26501	6.33763	0.628388	16.2914
β_{13} (AC)	-5.5565	6.33763	0.420082	16.2914
β_{23} (BC)	-.50425	6.33763	0.462323	16.2914

[a]: coefficients in red are not statistically significant.

Table 6. Analysis of Variance (ANOVA) for response surface model^[a]

	DF	SS	MS (variance)	F	p-value	SD
Total	15	77628.5	5175.23			
Constant	1	64080.2	64080.2			
Total corrected	14	13548.3	967.734			31.1084
Regression	2	11783.8	5891.88	40.0688	0.000	76.7586
Residual	12	1764.53	147.044			12.1262
Lack of Fit (Model error)	10	1764.17	176.417	998.409	0.001	13.2822
Pure error (Replicate error)	2	0.353397	0.176698			0.42035

[a]: $R^2=0.870$; DF=degree of freedom; SS=sum of squares; MS= mean Square; F value of the F-test between MSs; SD= standard deviation

The impact of “temperature” and “catalyst weight” on the WCO conversion is displayed in the surface and contour plot shown in Figure 11. A plausible explanation

of the negligible influence of reaction time on the final WCO conversion could be the little range set for “reaction time” applied in the experiments. As displayed in Figure 11, the conversion increases with the increase of temperature and reaction time, as predictable,³³ and good conversions ($>90\%$) were obtained already at about 120°C , confirming the results reported in Table 4. On the other hand, Figure 11 shows that the amount of catalyst could be decreased down to approximately 250 mg, but the temperature required to get high conversion must be as high as 140°C .

The optimal reaction conditions (quantitative conversion with the lowest possible factor values) were found by the MODDE13 software program as: 380 mg of catalyst, reaction temperature of 134°C and 18 min reaction time. These conditions are indicated by the black circles in the contour plot shown in Figure 11.

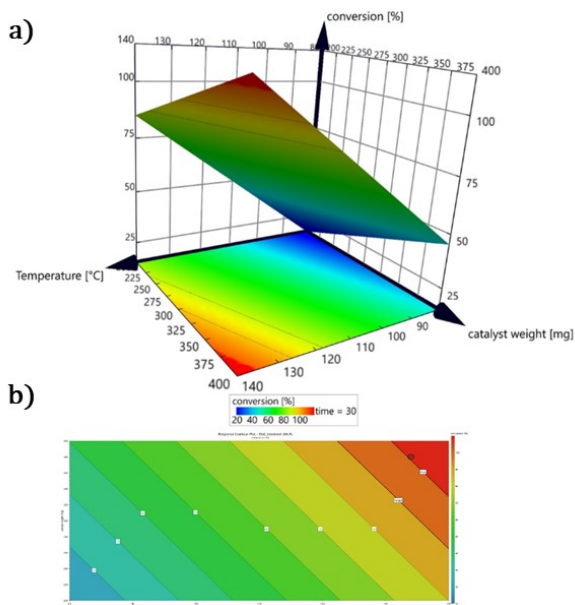


Fig. 11 - Three-dimensional (3D) response surface plot for the effect of temperature and catalyst weight on WCO conversion (reaction time = 30 min); b) contour plot at reaction time of 18 min.

Experimental tests were carried out both at the optimal reaction conditions ($T=134^{\circ}\text{C}$, $t=18$ min, 380 mg of SS) and at the conditions found by the software by imposing the amount of SS as high as 200 mg ($T=140^{\circ}\text{C}$, $t=45$ min). In both cases quantitative WCO conversions was reached (97.4% and 97.2 %, respectively) confirming the goodness of DoE predictions.

For all experiments, FAMES composition of the obtained transesterification blend was very similar, with methyl oleate (C18:1) and methyl linoleate (C18:2) as major components, followed by methyl palmitate (C16:0) and methyl stearate (C18:0) (Figure 12). Traces of methyl arachidate (C20:0) and methyl behenate (C22:0) were also detected.

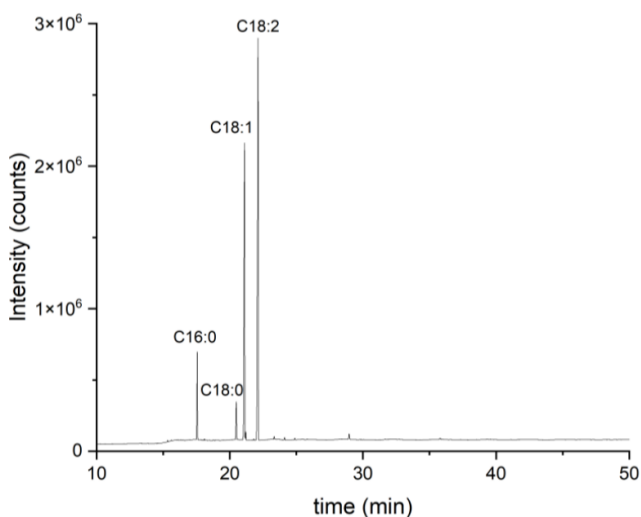


Fig. 12 - Representative GLC-FID chromatogram of the obtained FAMES

2.5 Recyclability Tests

Recyclability tests on the recovered catalyst were carried out to evaluate the possibility of reusing SS for several subsequent runs. The obtained results are summarized in Table 7.

By carrying out the MW-assisted transesterification of WCO under conditions ensuring quantitative conversion ($T=110\text{ }^{\circ}\text{C}$, $t=20\text{ min}$, $\text{SS}=400\text{ mg}$, entry 1, Table 7), the activity of the recovered SS dramatically dropped in the second and third runs (entries 2 and 3, Table 7), giving 41% and 31% conversion, respectively.

Aiming at removing possible adsorbed organic product which could deactivate the catalyst,³⁰ SS recovered after three subsequent runs was suspended in

methanol and sonicated for 30 min. Afterwards, the suspension was centrifuged (4000 rpm, 15 min), the liquid phase was removed and the solid catalyst was dried in the oven at 80°C overnight, before being employed for a “fourth cycle”, still leading to an unsatisfactory 33% conversion (entry 4, Table 7). To definitively rule out the presence of organic compounds on the surface of the recovered catalyst that could cause the observed decrease in its activity in the second cycle, reactions using ethyl octanoate (instead of WCO) as a substrate soluble in methanol were performed (conditions for each reaction: 400 mg SS, 922 mg ethyl octanoate, 10 mL CH₃OH, 110°C, 20 min). Subsequently, two recycle tests were carried out: one using ethyl octanoate again and another using WCO as the substrate. The conversions achieved in the recycle with WCO and ethyl octanoate were 24% and 22%, respectively (entries 6 and 7, Table 7), suggesting that the diminution of the catalytic activity with the recycles was not related to the presence of organic compounds on the surface of the recovered catalyst but rather to the nature of the catalyst itself.

With the aim of promoting the solubilization of catalytically active alkaline hydroxides from SS, the second run was carried out using a CH₃OH/H₂O=9/1 mL/mL solvent mixture. Unfortunately, only 16% conversion was registered (entry 8, Table 7), presumably because of the well-known detrimental effect of water on transesterification reactions.

Table 7. Results of recycling tests.

Entry	Run	Conv. of WCO (%)
1	First cycle	>95
2	Second cycle	41
3	Third cycle	31
4 ^[a]	Fourth cycle	33

5 ^[b]	First cycle (substrate: ethyl octanoate)	65
6 ^[c]	Second cycle (substrate: WCO)	24
7 ^[b,c]	Second cycle (substrate: ethyl octanoate)	22
8 ^[d]	Second cycle	16

Reaction conditions: 1.0 mL (922.1 mg) of WCO, 10 mL of CH₃OH and SS (400 mg) were stirred under MW irradiation at 110 °C for 20 min. [a]: SS sonicated in CH₃OH before the 4th run; [b]: ethyl octanoate (922.1 mg) as the substrate; [c]: recycle of entry 5; [d]: recycle of entry 1 performed in CH₃OH/H₂O=9/1 mL/mL

Recyclability tests carried out by using the optimal conditions predicted by DoE, (134 °C, 18 min, 380 mg) gave results comparable to those discussed above. In fact, as shown in the green histogram of Figure 13, the conversion went from 97% in the first cycle to 63% and 52% in the second and third cycles, respectively. To check whether a longer reaction time might guarantee quantitative conversions also in the recycles, a first cycle at T=110 °C were conducted with a reaction time of 45 min (with 400 mg of SS), and a second and third cycles at the same temperature (110 °C) but with a longer reaction time (3 h), obtaining quantitative conversions for each cycle (blue histograms in Figure 13).

Given that DoE indicated temperature as the most influential variable, a recyclability test was performed by carrying out a first cycle at 110 °C for 45 min (with 400 mg of SS), and a second cycle at higher temperature (140 °C) for the same time (45 min). Also in this case, quantitative conversion was achieved in the recycle test (red histograms in Figure 13) suggesting that quantitative conversion of the substrate can be achieved also in the recycles, provided that the subsequent cycles be performed at higher temperature or for longer time with respect to the first cycle.

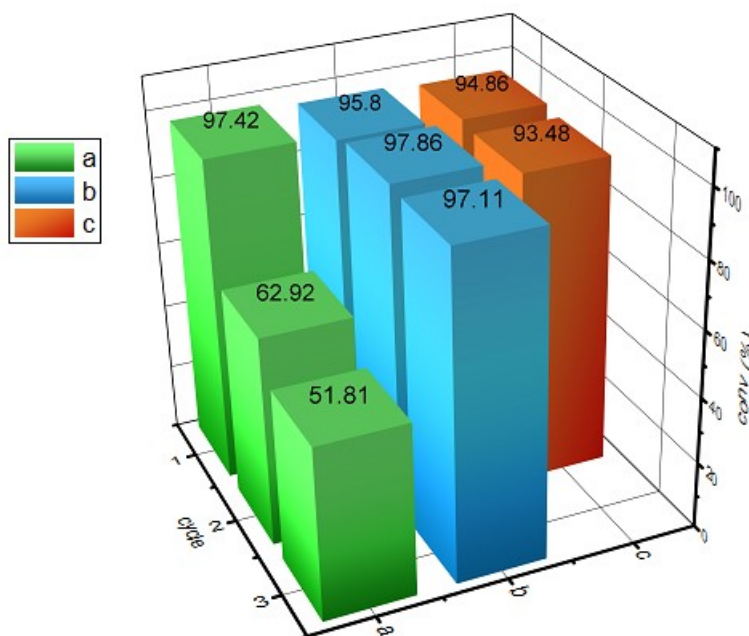


Fig. 13 - Recyclability tests of waste SS: a) $T=138\text{ }^{\circ}\text{C}$, SS weight = 380 mg, $t=18$ min for three cycles; b) first cycle: $T=110\text{ }^{\circ}\text{C}$, SS weight = 400 mg, $t=45$ min; second and third cycle: $T=110\text{ }^{\circ}\text{C}$, SS weight = 400 mg, $t=3$ h; c) first cycle: $T=110\text{ }^{\circ}\text{C}$, SS weight = 400 mg, $t=45$ min; second cycle: $T=140\text{ }^{\circ}\text{C}$, SS weight = 400 mg, $t=45$ min.

To investigate possible modifications of the SS occurring during the first run, which might be responsible for the drop-in activity during the recycles, the SS after duty has been analyzed by FT-IR (Figure 14), SEM (Figure 15), SEM/EDX (Figure 16) and XRF (Table 8). Results reported reveal that no significant change could be registered by all these techniques.

Table 8. List of main elements identified by XRF analysis.

Element	Weight % (pristine SS)	Weight % (SS after 1st cycle)
Si	3.8 ± 0.2	3.9 ± 0.2
Ca	31 ± 2	30.1 ± 1.7
Mn	4.7 ± 0.4	4.7 ± 0.4
Fe	18.8 ± 1.4	18.2 ± 1.5

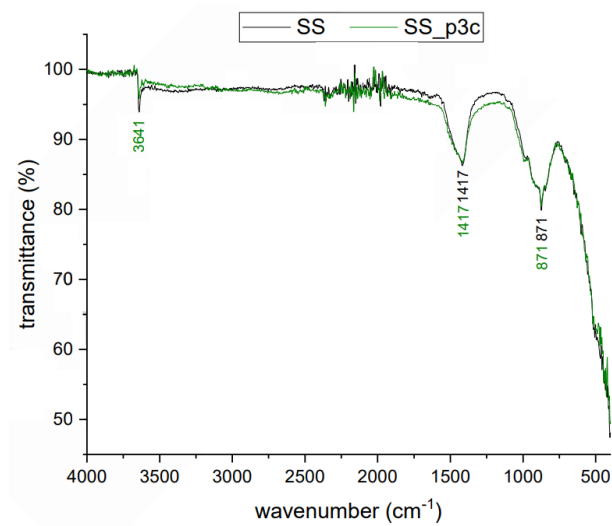


Fig. 14 - ATR-FT spectra of pristine steel slags (SS) and SS recovered after three cycles (SS_p3c)

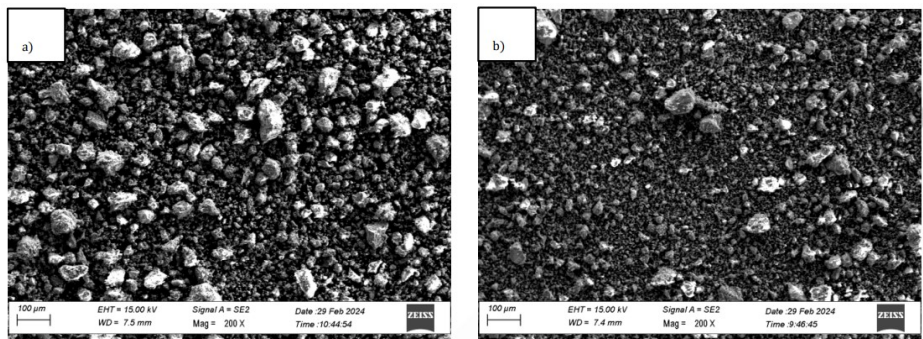


Fig. 15 - SEM micrographs of a) pristine steel slags b) steel slags after three cycles

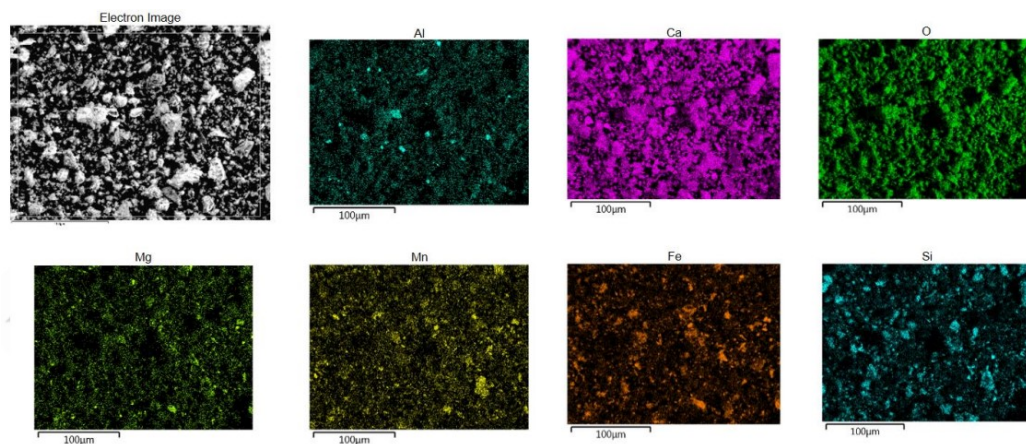


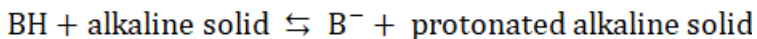
Fig. 16 - SEM/EDX mapping of steel slags after three cycles

2.6 Alkaline Tests on SS

Steel slags act as active catalyst for the transesterification reaction because of their high alkalinity.⁷⁶ The alkalinity (or acidity) of a solid could be defined considering the basic (acid) strength of the basic (acid) sites and/or considering the density of the basic (acid) sites onto the solid surface. The latter property can be evaluated using different methods such as a direct titration,⁷⁷ while the basic (acid) strength is usually evaluated using the Hammett indicator method.⁷⁸ This method consists of the addition of a solution of a pH indicator dissolved in an organic solvent onto a solid and the basic strength is expressed by an acidity function (H_0) defined as:

$$H_0 = pK_{BH} + \log \frac{[BH]}{[B^-]} \quad \text{Equation 4}$$

where $[BH]$ and $[B^-]$ are the concentrations of the indicator and its conjugated base, respectively, while pK_{BH} is the cologarithm of the dissociation constant of the indicator used.^{79,80} The process taken into account is the ability of the solid to deprotonate the indicator and to create its conjugate base:



In the Hammett indicator method few drops of a suitable indicator are poured onto the solid sample under investigation. If the adsorbed indicator assumes the color of its alkaline form, it means that the $[\text{B}^-]$ is higher than the $[\text{BH}]$ and the consequent H_0 will be higher than the pK_{BH} : therefore, the solid is more alkaline than the indicator ($H_0 > pK_{\text{BH}}$). Conversely, if the adsorbed indicator assumes the color of its acidic form, H_0 is lesser than the pK_{BH} and the solid is less alkaline than the indicator.

In the present study the Hammett indicator method was applied to evaluate the alkalinity of SS before and after catalysis choosing phenolphthalein as the reference indicator. In fact, phenolphthalein is easily available and has a pK_{BH} value of 9.5 ± 0.2 . Thus, the indicator turns from colorless to fuchsia at a pH of about 9.5. A net fuchsia color appeared in the Hammett test performed on pristine SS and this bright color was also visible in the halo of the dried liquid around the solid (Figure 17). This suggests not only that the H_0 of pristine SS is greater than 9.5 but also that soluble alkaline species are leached from SS to the indicator solution.

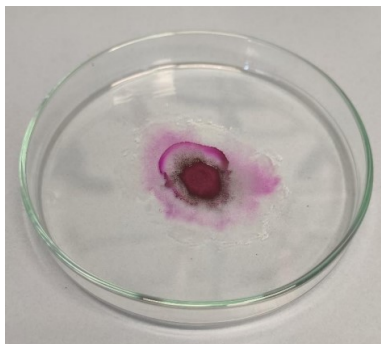


Fig. 17 - Hammett test performed on pristine SS

Hammett test performed simultaneously on pristine SS and recycled SS recovered after three cycles gave the same result (bright turning to fuchsia of both the solid and the surrounding halo) but the color change appeared after ca. one minute in

the case of pristine SS and after ca. two minutes in in the case of recycled SS (Figure 18).

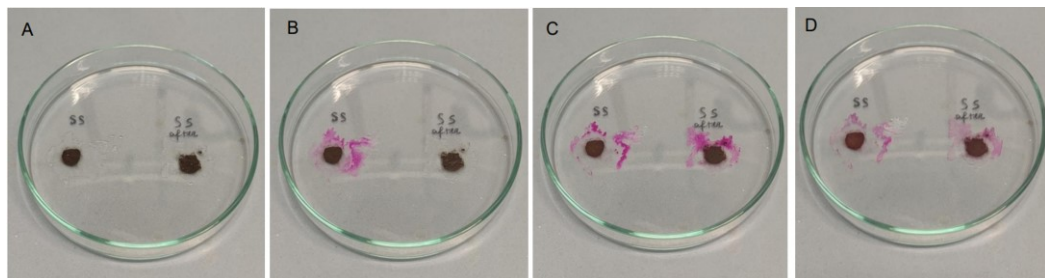


Fig. 18 - Four frames showing the Hammett test performed on pristine steel slags (on the left in the glass plate) and on SS recovered after three cycles (on the right). A: $t = 0$ s; B: $t = 90$ s; C: $t = 180$ s; D: $t = 240$ s

Recording UV-Vis spectra of the supernatant solution obtained after addition of 2.0 mL of concentrated phenolphthalein on 15 mg of pristine or recycled SS showed that the color change of the methanol solution after two days (evidenced by the appearance of the absorption peak at $\lambda = 552$ nm) after two days was much more pronounced in the case of pristine SS (the normalized absorbance at $\lambda = 552$ nm after two days was $4.7 \cdot 10^{-3}$ for pristine SS and $9.4 \cdot 10^{-4}$ for recycled SS) (Figure 19). However, after five days the intensity of the color for the two samples was the same (absorbance = 0.015).

The results of these experiments suggest that SS have high basic strength ($H_b > 9.5$) both as pristine and as recycled solid and that in both cases they act as a source of soluble alkaline species (presumably hydroxides) when suspended in methanol, the only difference being their “releasing time” into solution.

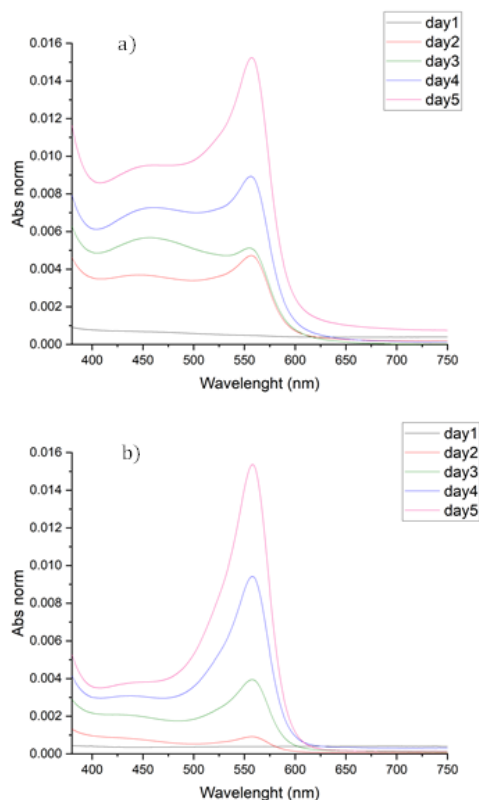


Fig. 19 - Hammett test on steel slags: UV-Vis spectra recorded at different times of the phenolphthalein solution in MeOH put in contact with a) pristine SS; b) SS recovered after three catalytic runs. The peak responsible for the fuchsia colour is at $\lambda = 552$ nm. The absorbance was normalised by dividing the absorbance value by the mass of SS in mg.

2.7 XPS Analyses

XPS measurements provide qualitative and quantitative information on the species present onto the surface of the sample and are therefore a powerful tool for characterizing a heterogeneous catalyst. Pristine and recycled SS were subjected to XPS analyses. A substantially homogeneous elemental composition on the surface was ascertained by comparing XPS wide scans recorded in three different sample points. An indicative element detected in all samples was carbon, whose XP C_{1s} spectrum (Figure 20) was curve-fitted and resulted in four peak components, the most in-

tense being the -C-C , -C-H peak and the CO_3^{2-} peaks. A close inspection of C_{1s} curve-fitting, $\text{Ca}2p_{3/2}$ Binding Energy (BE), and combination with XPS surface atomic percentages summarized in Table 9 revealed that Ca/CO_3^{2-} peak ratio was approximately equal to 1 for all samples, suggesting that calcium on the surface was in the form of calcium carbonate.

Moreover, the amount of CaCO_3 remained constant over recycles and no loss of surface calcium was observed. Another observation regards the amount of surface %Na which significantly decreased over cycles (Figure 21 and Table 9): the loss of Na as sodium carbonate can be excluded based on the carbonate peak component consistency. Moreover, considering the BE of $\text{Na}1s$, curve-fitted $\text{O}1s$, and $\text{Ca}2p_{3/2}$ peak components, it cannot be excluded the presence of sodium and/or calcium hydroxides on the surface of the three samples, as also confirmed by the O-H peak detected in the FT-IR spectrum. The ensemble of experimental evidence seems to suggest that leaching of sodium hydroxide from the catalyst surface into reaction solution probably occurs over cycles and is responsible for the catalytic activity of SS. Another important observation is related to the difference of composition between the surface of pristine SS (Table 9) with respect to the composition of the bulk SS (Table 2), suggesting that the majority of Na is onto the surface of the catalyst, while the majority of Fe is located in the inner part of the samples.

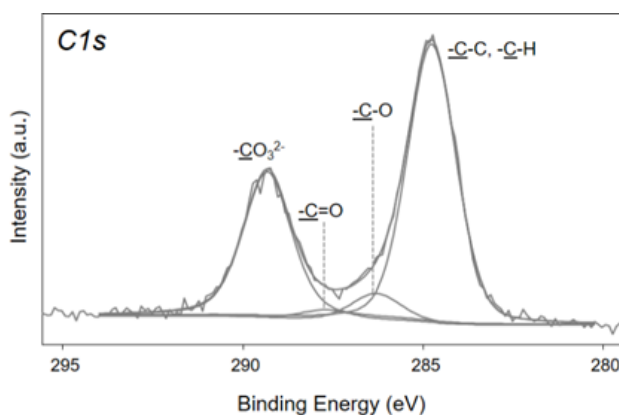


Fig. 20 - Signal of C_{1s} and its deconvolution of pristine SS. Similar spectra were obtained for SS_p1c and SS_p3c

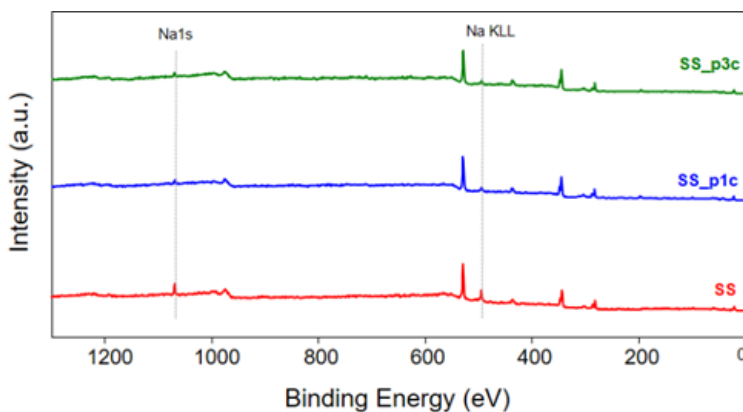


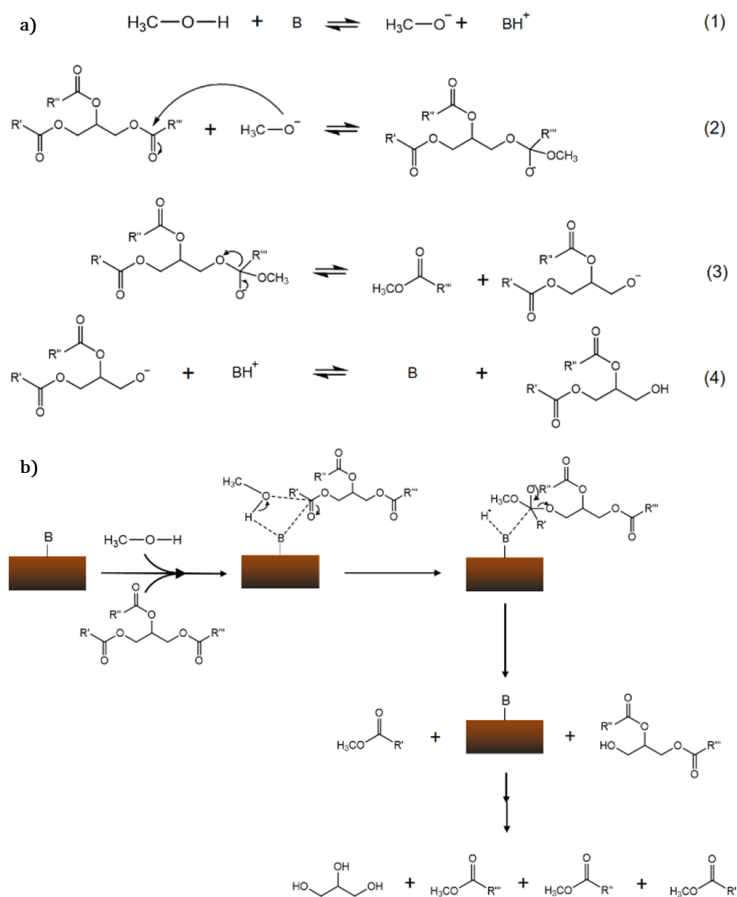
Fig. 21 - XP wide scan spectra of pristine SS (SS), SS after the first cycle (SS_p1c) and SS after the third cycle (SS_p3c). Na1s and NaKLL signals are marked

Table 9. Atomic elemental percentages of the elements detected by XPS analyses. Data are reported as mean values $\pm 1S$.

Sample	%C-C	%C-O	%C=O	%CO ₃ ²⁻	%O	%Na	%Si	%Ca	%Fe	Ca/ CO ₃ ²⁻
SS	15.8 $\pm$ 2.8	1.6 $\pm$ 0.3	0.7 $\pm$ 0.1	9.9 $\pm$ 0.9	50.2 $\pm$ 1.9	8.7 $\pm$ 0.7	3.1 $\pm$ 0.3	9.2 $\pm$ 0.4	0.9 $\pm$ 0.4	0.9 $\pm$ 0.1
SS_p1c	22.1 $\pm$ 1.1	3.3 $\pm$ 0.5	0.9 $\pm$ 0.3	9.3 $\pm$ 0.4	44.6 $\pm$ 0.7	3.2 $\pm$ 0.1	3.4 $\pm$ 0.6	9.9 $\pm$ 0.5	1.4 $\pm$ 0.1	1.1 $\pm$ 0.1
SS_p3c	25.4 $\pm$ 0	3.7 $\pm$ 0.6	1.0 $\pm$ 0.1	7.9 $\pm$ 1.0	43.1 $\pm$ 1.8	2.4 $\pm$ 0.3	3.9 $\pm$ 1.0	9.6 $\pm$ 1.0	1.4 $\pm$ 0.2	1.2 $\pm$ 0.1

2.8 Considerations on Mechanism

The difference in elemental composition of the catalyst surface with respect to the bulk and the variation of surface Na content over the reaction cycles can give some insights into the reaction mechanism. Alkaline tests and XPS analyses indicated for the catalytic activity of SS in the alkaline transesterification of WCO the probable coexistence of a double mechanism consistent with the presence of synergic homogeneous (Scheme 1a) and heterogeneous (Scheme 1b) pathways.



Scheme 1- Proposed mechanism for WCO alkaline transesterification catalyzed by SS: a) homogeneous and b) heterogeneous pathway.

It could be assumed that in the homogeneous way SS acted as a reservoir of small amount of catalytically active sodium hydroxide that could emerge from the inner part of the already employed catalyst in more difficult way with respect to pristine SS, requiring higher temperature or longer time to be leached into solution compared to the first run. Moreover, in the heterogeneous pathway the basic sites of the catalyst surface could assist both the nucleophilic attack of the carbonyl carbon and the alkoxide formation (Scheme 1b).⁸¹

2.9 Conclusion

An innovative and sustainable procedure is proposed for the synthesis of bio-diesel starting from WCO in the presence of waste steel slags as catalyst under microwave irradiation. The developed protocol allowed the use of milder reaction conditions than conventional methods. Response surface method based on Box-Behnken design indicated temperature and catalyst weight as the most influential variables. The mathematical model calculated by the software afforded the optimal conditions for achieving quantitative conversion of WCO in only 18 minutes, a time much shorter than the several hours requested by conventional heating. Alkaline tests and XPS analyses suggested the coexistence of heterogeneous and homogeneous mechanisms for the catalytic activity of SS in the alkaline transesterification of WCO. The homogeneous mechanism originates by the leaching of catalytically active methanol soluble species (presumably, sodium hydroxide) while the heterogeneous mechanism is mediated by the basic sites present onto the SS surface. Recyclability tests showed a drop of catalytic activity that can be overcome by increasing the reaction temperature or time. A different elemental (Na) composition of the catalyst surface with respect to its inner zone was observed, that might be responsible for the observed changes of SS catalytic activity. In fact, the amount of surface sodium decreased over the catalytic cycles. The developed MW-assisted procedure for preparing bio-diesel from a waste (WCO) employing a waste (SS) as the catalyst could open new perspectives in the field of biofuels according to circular economy principles.

2.10 Experimental Section: Analytical Techniques

Elemental analyses on SS were carried out with a portable energy dispersive X-ray fluorescence spectrometer (P-ED-XRF, NITON™ XL3 t, Thermo Scientific, Waltham, USA) equipped with an Ag collimator source (50KeV and 40 μ A), and a large SSD detector (energy resolution < 160 eV @Mn–K α). Scanning Electron Microscopy (SEM) analyses were carried out by employing a FESEM Zeiss sigma 300 VP (Zeiss Oberkochen, Germany) to observe the surface morphology of the samples at 15 kV,

using a carbon-covered electron microscopy specimen holder. Chemical composition and elemental mapping were determined by Energy Dispersive X-ray Analysis (EDX) under SEM observation.

Thermogravimetric analyses (TGA) were performed using a Hitachi STA 7200 instrument fluxed with nitrogen (100 mL/min). The method involved an initial equilibration step at 50 °C and then a temperature ramp from 50 to 800 °C with a heating rate of 10 °C/min. X-ray powder diffraction data were collected in air using a PANalytical Empyrean X-ray diffractometer with Bragg-Brentano geometry, large beta filter-Nickel, detector (PIXcel3D) and CuK α radiation, operating at 40 kV/40 mA. The X-ray data were collected in the 2 θ range 10–90° (step size 0.026, Scan Step Time 996.54 s). The diffraction patterns were processed using the PANalytical B.V. software HIGHScore Plus version 3.0e. To determine the crystallite size of the identified phases, a LeBail analysis was performed using Profex version 3.5.0⁸²

Transesterification experiments were carried out in an ETHOS ETOUCH Milestone microwave applicator. Liquid gas-chromatography (LGC) analyses were carried out with an Agilent 7890 GC equipped with a Flame Ionization Detector (FID) fueled by hydrogen and air. The employed column was the DB-FastFAME (90 m $\times$ 0.25 mm $\times$ 0.25 μ m) and the gas carrier was helium. Surface elemental and chemical speciation analyses were performed with a Versa Probe II Scanning XPS Microprobe spectrometer (Physical Electronics GmbH) using a monochromatized AlK α source with an X-ray spot size of 200 μ m and a power of 47.6 W. Wide scans and detailed spectra were acquired in Fixed Analyzer Transmission (FAT) mode with a pass energy of 117.40 eV and 46.95 eV respectively. An electron gun was used for charge compensation (1.0 V, 20.0 μ A). All binding energies were referenced to C1s at 284.8 $\pm$ 0.1 eV for adventitious hydrocarbon. Data processing was performed using MultiPak software v. 9.9.0.8, 2018. Each analysis was performed in three different sample points.

FT-IR spectra (in attenuated total reflectance, ATR mode) were recorded on a Jasco FT-IR 4200 spectrophotometer. UV-Vis spectra were recorded on a dual beam Jasco V-670 spectrophotometer.

CHAPTER III

PARTIAL HYDROGENATION OF WASTE COOKING OIL BIODIESEL WITH STEEL SLAGS-BASED IRON OXIDES/NICKEL NANOCATALYSTS

3 PARTIAL HYDROGENATION OF WASTE COOKING OIL BIODIESEL WITH STEEL SLAGS-BASED IRON OXIDES/NICKEL NANOCATALYSTS

3.1 Introduction

Biodiesel, produced mainly through transesterification of vegetable oils or animal fats, is a promising alternative to fossil fuels due to its biodegradability and re-

duced environmental impact. However, the crude biodiesel obtained from this process is not immediately usable as a fuel due to inherent limitations, such as poor oxidative stability and suboptimal cold flow properties. To overcome these issues, an upgrading reaction must be carried out, which consists of a partial hydrogenation reaction of the polyunsaturated chains of FAMES with the objective of converting polyunsaturated compounds to monounsaturated ones while avoiding obtaining a fully saturated product. This balancing allows for greater oxidative stability without compromising cold flow properties. Nickel-based catalysts have proven effective in these reactions due to their activity, selectivity and relatively low cost. This chapter describes the investigations conducted using different nickel-based catalyst supported onto SS, highlighting the results and implications of this approach.

As mentioned before, steel slag represents an industrial by-product with high potential due to its unique chemical composition and versatility in numerous catalytic processes. In the present work, SS were used as a support for catalytically active nickel particles, with the aim of optimizing the quality of biodiesel obtained from waste cooking oil (WCO) through partial hydrogenation reactions of the unsaturations present on the FAMES chains.

This study is a natural extension of previous work, introducing a strategic modification of the SS to obtain a new catalyst effective in the biodiesel upgrading step. Several studies have demonstrated the effectiveness of nickel-based catalysts using steel slag as a support. For instance, in a study conducted by Zhang et al.,⁸³ a nickel (Ni)-based catalyst was loaded onto steel slag rich in metal oxides using the impregnation method. The study investigated the effects of the catalyst on hydrogen-rich gas production using sludge steam gasification. It highlighted how the impregnation method effectively facilitated the loading of nickel onto the slag support, significantly improving the production of hydrogen-rich gas.

In another study,⁸⁴ a nickel-based steel slag (SS) catalyst prepared via wet impregnation was used in catalytic reforming experiments with primary volatiles produced from the pyrolysis of pine sawdust. This study synthesized a bimetallic catalyst containing iron, which, due to a synergistic effect, enhanced catalytic activity both in

terms of tar conversion and reaction rate. Another study showed that steel mill slag can be effectively used to develop inexpensive, high-performance catalysts for biomass-derived tar reforming. Calcination at 900 °C resulted in the formation of Fe_2O_3 and MgFe_2O_4 , with NiO particles well dispersed on the surface of the nickel-enriched slag. The obtained catalysts showed high activity in primary tar removal and a significant increase in fuel gas production.⁸⁵ These results clearly highlight the potential of steel slag as support for nickel-based catalysts to be used in many hydrogen and gas producing reactions. The combination of the inherent chemical characteristics of steel slag combined with targeted modifications, such as impregnation and calcination, resulted in high-performance and sustainable catalysts for various applications.

In the present thesis, a bimetallic Fe-Ni system onto SS was synthesized aiming at combining the stability and basic properties of the support with the high catalytic activity of the metals, useful for biodiesel upgrading. Iron catalyst has been cited as a promising enhancer of nickel catalytic performance in Ni-Fe bimetallic combinations. Fe-Ni couplings have showed higher activity and stability than monometallic systems for hydrogenation of $\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{C}\equiv\text{N}$ bonds.⁸⁶ In work conducted by Naseeb Ullah et al,⁸⁷ Ni-Fe bimetallic catalysts (Ni_3Fe_1 BMNPs) have been shown to be a highly efficient solution for the reductive depolymerization of biomass into sugar alcohols. The synergistic combination of nickel and iron optimizes both the catalytic activity and selectivity of the process, minimizing undesirable secondary reactions such as hydrogenolysis and over hydrogenation. Iron acts not only as a promoter, improving the efficiency of nickel active sites, but also contributes to the stabilization of the bimetallic structure, ensuring good metal dispersion and preventing nanoparticle agglomeration. Bimetallic Fe-Ni/ SiO_2 catalysts have also been used for furfural hydrogenation in furfuryl alcohol, increasing both the activity and selectivity of Ni,⁸⁸ for hydrogenation of carbon monoxide over SiO_2 ,⁸⁹ and in other different hydrogenation reaction.^{90,91} Furthermore, a study has been conducted exploring the relationship between the catalytic activity of Ni-Fe bimetallic catalysts and the metal-hydrogen binding energy (H binding energy) during hydrogenation reactions of $\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{C}=\text{N}$ double bonds. Catalytic activity resulted inversely related to metal-hydrogen binding energy.

Pure Ni is an excellent catalyst for dihydrogen dissociation, but excessive nickel-hydrogen bond energy and poor selectivity are the main limitations. In Ni-Fe catalysts, the addition of Fe changes the nickel-hydrogen bond energy, optimizing the transfer of hydrogen atoms to the substrates. In a Ni-Fe catalyst (Ni/Fe molar ratio equal to 2), for example, the nickel-hydrogen bonding energy resulted reduced, promoting greater catalytic activity and selectivity than in pure nickel catalyst. With monometallic Ni, the strong binding energy can result in excessive hydrogen accumulation on the surface, slowing the transfer of hydrogen atoms to reactive substrates.

In the present thesis, two methods for partial hydrogenation were employed: the conventional partial hydrogenation method using molecular hydrogen (H_2) and the catalytic transfer hydrogenation (CTH) method using $NaBH_4$ as the hydrogen donor. Both methods utilized heterogeneous nickel-iron based catalysts supported on modified SS.

So, apart from the catalysts composition, the synthesis method is another crucial factor that significantly affects catalyst performance.⁹² Among the various approaches available, the impregnation method stands out for its flexibility and simplicity, making it one of the most commonly used methods for preparing nickel (Ni)-based catalysts.⁹³

This chapter describes the experimental details and results obtained, helping to define the role of modified SS as versatile and low-cost catalysts for sustainable chemical processes.

3.1.1 Biodiesel properties

The physicochemical properties of biodiesel are closely linked to the structural configuration, composition, and type of fatty acid methyl esters (FAME). Biodiesel produced from different raw materials contains different fatty acid compositions,⁹⁴ and this difference leads to variations in the chemical and physical properties of the biofuel product.⁹⁵

Fatty acid esters primarily differ for the number of double bonds present in their chains. They can be classified as saturated or unsaturated, with unsaturated fat-

ty acids further divided into monounsaturated and polyunsaturated.⁹⁶ Saturated fatty acids have no double bonds between carbon atoms, such as myristic acid (C14:0), palmitic acid (C16:0), and stearic acid (C18:0). Monounsaturated fatty acids contain a single double bond along the carbon chain, such as palmitoleic acid (C16:1) and oleic acid (C18:1). Polyunsaturated fatty acids contain at least two double bonds along the carbon chain, such as linoleic acid (C18:2) and linolenic acid (C18:3).

In both edible and non-edible oils, the main fatty acid triglycerides are made of oleic acid (C18:1), linoleic acid (C18:2), palmitic acid (C16:0), and stearic acid (C18:0).⁹⁷

When biodiesel is produced, its FAMES have such proportions that it cannot be used as a fuel by itself, but as a blend with conventional diesel. Two main challenges, in particular, are related to the application of pure biodiesel in compression ignition (CI) engines: inadequate cold flow characteristics and oxidative instability directly correlated to the presence of both saturated and unsaturated fatty acids.⁹⁸ In general, cold flow properties improve passing from saturated FAMES to monounsaturated FAMES and then to polyunsaturated FAMES (Figure 22, red curve). In contrast, oxidative stability follows an opposite trend, being better in saturated FAMES and progressively decreasing in polyunsaturated FAMES (Figure 22, blue curve).

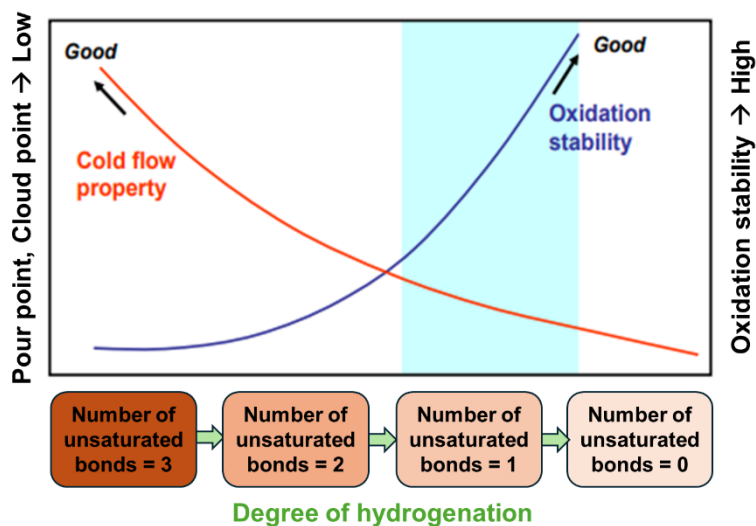


Fig. 22 - Trend of cold flow properties and oxidative stability of FAMES in biodiesel as a function of the degree of saturation

In cold conditions, biodiesels with high levels of saturated fatty acids tend to solidify, causing operational problems in engines, such as clogging of pipes, filters and injectors. This limitation reduces its marketability, especially in countries with harsh climates. Saturated fatty acids, solidify easily even at room temperature because of their linear and compact molecular structures, which can arrange and pack well⁹⁹ and favour organization into crystals. In contrast, unsaturated FAMES, have irregular and folded molecular structures that are more difficult to pack, thus reducing the tendency to solidify. For this reason, biodiesels composed mainly of unsaturated, short-chain, branched fatty acid esters need to be upgraded to improve their low-temperature behaviour. However, the presence of a high amount of unsaturated fatty acids will increase the possibility that biodiesel undergoes to auto-oxidation, polymerization and rancidity. In the literature, among all known unsaturated fatty acids, linolenic and linoleic acids show a greater tendency for auto-oxidation, which reduces the oxidative stability of biodiesel.⁹⁵ Consequently, the mono-unsaturated FAME is a valuable component for high-quality biodiesel with good oxidation stability and cold flow

properties, especially the *cis*-isomer of C18:1 (methyl oleate).¹⁰⁰ Quality standards have been introduced to regulate the production, storage and distribution of biodiesel, with the aim of protecting consumer rights and ensuring a high level of product quality.¹⁰¹ Serving as worldwide reference, American or United States (US) standard ASTM D6751 and European (EU) standard EN14214 are the most widely referred standards. There are significant differences between them. For example, the U.S. standard accepts both fatty acid methyl esters (FAMES) and fatty acid ethyl esters (FAEEs), while the European standard allows only FAMES.¹⁰¹ Generally, most of these standards include common limits for biodiesel properties, such as oxidative stability, iodine number and cold filter plugging point. According to COMMISSION REGULATION (EU) 2022/2383 of Dec. 6, 2022,¹⁰² pure B100 biodiesel must meet the parameters of oxidative stability OS<8h, CFPP<10°C, and IV iodine value <120 g iodine/100g. (Table 10)

Table 10. Key parameters for pure B100 biodiesel according to REGULATION (EU) 2022/2383.

Parameter	Unit	Limit
Oxidation stability	h	<8
Cold filter plugging point	°C	>10
Iodine value	g iodine/100 g	<120

3.1.2 Cold flow properties of biodiesel

The cold flow properties of biodiesel, measured through parameters such as pour point (PP), cloud point (CP) and cold filter clogging point (CFPP) influence fuel behavior at low temperatures. These indicators determine when fuel loses its ability to flow or causes clogging in filters and injectors due to crystal formation.¹⁰³

- **Pour Point (PP):** Represents the minimum temperature at which the fuel retains its fluidity and is a crucial parameter in assessing its storage and distribution behavior. In other words, PP is an evaluation of biodiesel's fuel gelling point. It is an important parameter to evaluate flow behaviour of biodiesel in pipeline distributions and storages.⁹⁶

- **Cloud point (CP):** This indicates the temperature at which wax crystals begin to form, which can clog filters and injectors.⁹⁵

- **Cold filter plugging point (CFPP):** Measures the lowest temperature at which fuel can still pass through a standardized filter, providing a practical indication of operating limits.⁹⁵

At low temperatures, biodiesel crystallizes and condenses to a gel-like liquid. Crystallization of the fuel molecules continues within the liquid and requires sufficient thermodynamic force, generated by strong intermolecular interactions when the temperature drops below the melting point. The process (Figure 23) occurs in two main stages: nucleation and crystal growth. During nucleation, liquid molecules aggregate to form solid embryos (crystallites or crystal lattices). Next, the crystalline lattices grow as new layers are added, forming large crystals. This process continues until a network of high-melting-point crystals is created within the liquid. As the temperature drops further, the number and size of crystals (0.5^{-1} mm) increase, blocking fuel flow and causing engine starting problems.

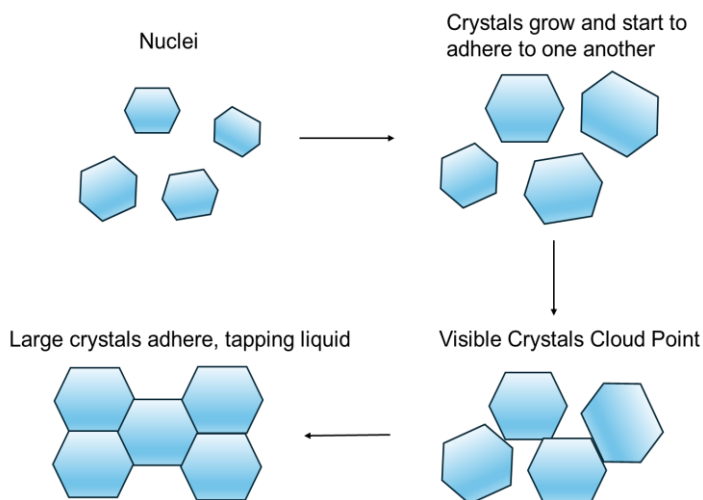


Fig. 23 - Crystallization process of biodiesel at low temperatures.

3.1.3 *Oxidation stability*

Oxidation stability indicates the propensity of biodiesel to degrade in the presence of light, moisture, and impurities.¹⁰⁴ Oxidation of biodiesel involves the generation of peroxides and hydroperoxides, which further decompose into simpler molecules such as ketones, aldehydes, alcohols and low molecular weight acids.¹⁰⁵ For biodiesel, oxidative stability is a crucial issue because it involves the production of harmful byproducts that impair engine operation. Unstable fuel can form deposits, residues and sediments, increasing viscosity. Oxidation of biodiesel is promoted by the presence and position of double bonds (degree of unsaturation) in fatty acid molecules, especially bis-allyl bonds. The double bonds of unsaturated fatty acids increase reactivity with oxygen, especially when the molecules are exposed to moisture or air. Polyunsaturated fatty acids are more prone to oxidation than monounsaturated fatty acids due to the allyl methylene structure.¹⁰⁶

Most natural fatty acids are polyunsaturated and exhibit an interrupted methylene configuration, characterized by the presence of multiple *cis* double bonds separated by a single methylene unit ($-\text{CH}_2-\text{CH}-$).¹⁰⁷ These interrupted methylene structures are generally less stable than their conjugated isomers, which, on the contrary, show more robustness due to the delocalization of π electrons, which confer partial stability to the structure. The bis-allyl sites present in polyunsaturated fatty acids are particularly vulnerable to oxygen exposure, making them prone to oxidation.¹⁰⁸ For example, linoleic acid and methyl linoleate, with carbon-carbon double bonds at positions 9 and 12, generate a bis-allyl site at position 11. Because the hydrogen in the bis-allyl site can be easily removed in the initial phase of oxidation, this site is weaker and therefore more susceptible to oxidative attack than normal allyl sites (Figure 24).¹⁰⁸

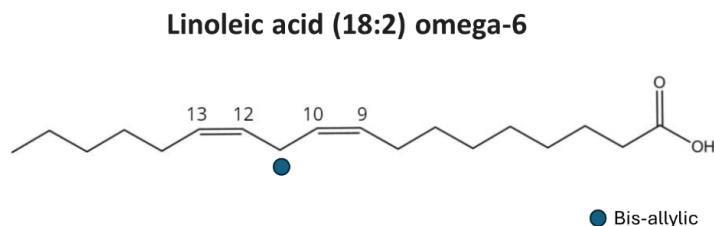


Fig. 24 - Bis-allylic site in the structure of linoleic acid. The carbon-carbon double bonds at positions 9 and 12 generate a bis-allylic site at position 11.

The oxidative stability of biodiesel is determined by chemical reactions divided into two main phases: primary oxidation and secondary oxidation. In the primary oxidation there are three phases: initiation, propagation and termination. During initiation, free carbon radicals ($R^\cdot$) are formed, which react rapidly with oxygen to generate peroxide radicals ($ROO^\cdot$) and hydroperoxides ($ROOH$). Propagation continues as new radicals are formed, exponentially increasing the byproducts. Termination occurs when the free radicals react with each other, forming stable products. In secondary oxidation stage, which is also known as vinyl polymerization process, hydroperoxides decompose to produce aldehydes (propanals, hexanals and heptanals), aliphatic alcohols, formic acid and formate esters which affect the biodiesel characteristics. Short chain free fatty acids are also formed at this stage which resulted in increased acidity of biodiesel. In both stages (primary and secondary), oxidation reaction continues until reactive sites of the fatty acid molecules are completely exhausted.

The oxidative stability of biodiesel can be measured by the Rancimat method (EN 14112) or the oxidative stability (OS) index. Both methods for determining the induction period are quite similar. Through these methods, the biodiesel sample is heated up to 110 °C in a sealed tube. Air is passed through the sample for oxidation to occur. The gas released (primary products) from the sample is then passed through distilled water in a tube equipped with a conductivity meter. The conductivity is then monitored continuously for any sharp increase. A sharp increase in conductivity indicates the formation of short-chain carboxylic acids (secondary oxidation

products) such as formic acid and acetic acid, which are soluble in water. The induction period (IP) is taken when there is a sharp increase in conductivity.¹⁰⁷

3.2 Biodiesel upgrading

Recent technological developments have focused on improving biodiesel properties. Biodiesel upgrading is achieved through the partial hydrogenation of polyunsaturated FAMES,^{37,109} toward *cis*-monounsaturated FAMES aiming at achieving the highest possible oxidative stability and, at the same time, at maintaining good cold flow properties. The hydrogenation process can be carried out by two methods that differ in the supply of hydrogen. The most common is that hydrogen is supplied directly as molecular hydrogen in gaseous form, while the other is that hydrogen is supplied by a compound that acts as a donor during the reaction, which is called catalytic transfer hydrogenation.¹¹⁰ Achieving the ideal outcome through partial hydrogenation poses challenges. During the hydrogenation of polyunsaturated FAMES, the monounsaturated FAMES in biodiesel may also undergo hydrogenation, potentially leading to a biodiesel rich in saturated FAMES, which lacks the desired properties. Additionally, *cis*-monounsaturated FAMES may isomerize into their *trans* isomers during the process, degrading fuel quality by reducing cold flow properties below acceptable standards. The extent of these undesired reactions depends significantly on the catalytic system and operational conditions chosen for hydrogenation. Therefore, the success of biodiesel upgrading requires a catalytic system and conditions that selectively hydrogenate polyunsaturated FAMES into *cis*-monounsaturated FAMES while minimizing isomerization and complete hydrogenation.

As already highlighted, partial hydrogenation of FAMES can be conducted by employing different hydrogen sources, such as molecular hydrogen (H₂, conventional partial hydrogenation), or hydrogen *in situ* generated by catalytic systems employing hydrides, formic acid, branched alcohols, polyols and so on (catalytic transfer hydrogenation)

Conventional Partial Hydrogenation: refers to the process of biodiesel hydrogenation carried out using a heterogeneous catalyst and the use of molecular hydrogen (H_2) supplied in gaseous form as a reactant. This approach represents the traditional and most widely studied method for improving the properties of biodiesel, as evidenced by its wide application and documentation in the scientific literature. (Figure 25)

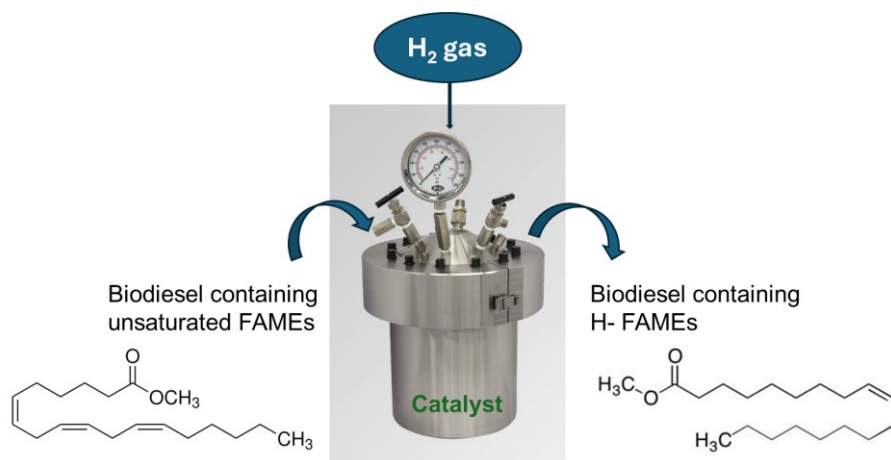


Fig. 25 - The conventional partial hydrogenation process.

Several alternative methods to conventional partial hydrogenation exist, each with unique advantages:

Catalytic Transfer Hydrogenation (CTH): in this method instead of being supplied as pure molecular hydrogen H_2 in gaseous form, the hydrogen is supplied through compounds that act as hydrogen donors^{110,111} e.g., formates, formic acid, secondary alcohols and also sodium borohydride ($NaBH_4$) which acts as a hydrogen storage material with a high hydrogen content.¹¹² The use of sodium borohydride as a hydrogen donor would provide a new way for hydrogenation of oils and fats.¹¹¹ CTH avoids the use of costly, hazardous hydrogen gas and operates under mild conditions, with cost-effective Ni catalysts preferred over noble metals like Pd and Pt.^{110,112} CTH utilizes the stable hydrogen donor, including cyclohexene, cyclohexadiene, hy-

drazine, phosphinic acid, sodium hypophosphite, and alcohols, to replace the explosive hydrogen gas.^{110,112}

The CTH method could employ a two-phase aqueous/organic system where the catalyst resides in the aqueous phase and FAMES in the organic phase. A very important feature of this method is the quantitative recovery of the catalyst with simple two-phase separation and its recyclability for continuous catalytic cycles without significantly reducing its activity and selectivity.^{113,114}

3.2.1 *Heterogeneous catalytic systems in partial hydrogenation reactions*

Biodiesel upgrading catalysts are mostly metal particles supported on porous materials consisting of carbon, silicon or aluminium materials.¹¹⁵ The metals most commonly encountered in catalytic systems are Pd,¹¹⁶ Pt¹¹⁷ and Ni,¹¹⁸ while there are few reports of upgrading attempts using metals such as Rh¹¹⁹ and Cu.¹⁰⁰ However, despite all the development and research in biodiesel upgrading, there is still a need to find more effective catalysts to allow biodiesel to be used either in blends with conventional diesel in higher proportions or as a stand-alone fuel without posing any risk to the vehicle engine.

It has been reported that in FAMES partial hydrogenation reaction catalysed by Pd, Pt and Ni supported catalysts, Pd system was the most effective among them, while Ni catalyst showed the lowest performance.^{120,121} However, it has been demonstrated that Pd caused the isomerization of *cis*-monounsaturated FAMES into *trans* isomers to a more significant extent.^{122, 123} As for Pt, it has been noted that it caused the complete hydrogenation of FAMES, leading to the production of biodiesel with higher amounts of saturated FAMES.¹²³ In addition to the nature of the metal, the efficiency and selectivity of the catalysts are affected by the size of the metal nanoparticles on the support surface. Tri- and di-unsaturated FAMES interact with metal nanoparticle surfaces more intensively than monounsaturated FAMES due to the presence of additional double bonds.¹²² Furthermore, the size of the catalyst nanoparticles can affect both activity and selectivity. In fact, in a study conducted by Numwong et al.¹²² on Pd/SiO₂ and Pd/MCM-41 catalysts, it has been observed that larger Pd particles (6.1-7.8 nm) offer planar surfaces that promote strong interaction with the conjugated

double bonds of polyunsaturated FAMES (C18:3 and C18:2), increasing catalytic activity but also promoting *cis-trans* isomerization. In contrast, smaller particles (2.7-4.0 nm) have a surface characterized by defects and kink-like sites, which limit interaction with isolated monounsaturated FAME double bonds (C18:1), thus reducing *cis-trans* isomerization, providing greater selectivity toward *cis*-C18:1, and improving the oxidative stability and cold flow properties of the final biodiesel. These results agree with other studies, which report that larger particles increase activity but promote isomerization of *cis*-monounsaturated esters towards *trans* isomers.^{120,121} In addition, the effectiveness of the catalyst correlates with the distribution of metal nanoparticles on the support, as catalysts with a more uniform dispersion of particles show higher activity.^{124, 125} The acidity of the catalyst surface is another crucial parameter. Catalysts with moderate or strong acidity show higher activity but lower selectivity toward *cis* FAMES.¹²⁶ Finally, even the morphology of the catalyst support affects activity and selectivity. Mesopores promote better contact with active sites than macro- and micropores, improving activity.¹²⁶ Furthermore, catalysts with fibrous morphology show significant activity and selectivity than due to good accessibility of the substrates towards active sites.¹²⁷

There are several mechanisms causing the deactivation of heterogeneous catalysts. They can be grouped into six primary categories of catalyst deterioration: (a) poisoning, (b) fouling, (c) thermal damage, (d) formation of volatile compounds and/or metal leaching from the catalyst surface to the solvent media, (e) vapor–solid or solid–solid interactions, and (f) attrition or crushing. The dominant deactivation mechanism depends on the specific reaction and catalyst system, and multiple factors may work together synergistically to affect the catalyst's efficiency.¹²⁸

3.2.2 Nickel-based catalysts in biodiesel upgrading reactions

Nickel-based supported catalysts are commonly used due to their lower cost compared to noble metal-based catalysts. Nickel represents one of the most common elements in metal catalysts.¹²⁹ It is the fourth most abundant transition metal on Earth, after iron, titanium and zirconium. Currently, its cost is around US\$3.8 per pound, a figure equal to about 1/5000th of the price of gold.¹²⁹ Nickel has a long tradition in

modern catalysis: its first application as a catalyst for hydrogenation reactions dates to the 19th century, an achievement that earned it the Nobel Prize in Chemistry in 1912. Subsequently, it has been discovered that nickel showed remarkable activity in a wide range of processes, especially in hydrogenation and reforming reactions. Despite the great success and numerous industrial applications of nickel-based catalysts, single-component variants still fail to fully meet the activity, selectivity, and stability requirements for many of the emerging new applications in the energy and environmental sectors.

Among the various catalysts used in the partial hydrogenation reaction of FAMES, those based on nickel play a particularly important role. However, monometallic Ni-based catalysts have demonstrated lower catalytic activity than bimetallic systems, failing to achieve conversion levels that would significantly improve biodiesel properties. For example, nickel catalysts supported on charcoal, such as Ni/C did not show satisfactory catalytic activity. In fact, the limited C18:1 increase obtained indicates that these catalysts are not yet able to effectively direct the reaction toward the desired product.^{130 131}

However, recent studies have shown that significant improvements in catalytic performance can be achieved through appropriate arrangements, such as the use of alternative supports or the addition of additional metals in combination with Ni. This has been highlighted, for example, by investigations conducted by Zhu et al.¹³² and Phumpradit et al.¹²⁷ who used Ni/betnite and Ni/electrospun silica fiber catalysts, respectively, and were able to achieve conversions of 75% and 71.3%.

Other metals are usually added to improve the catalytic activity of Ni-based systems, such as transition metals,¹³³ noble metals,¹³⁴ alkali metals¹³⁵ and alkaline earth metals¹³⁶ used principally in steam reforming reactions. Bimetallic catalysts, which often have different electronic and chemical properties than the starting metals, can offer greatly improved performance. Since the pioneering systematic studies conducted by Exxon Research and Engineering in the early 1960s, the range of bimetallic catalysts has expanded considerably, especially in the past two decades. Among all bimetallic catalysts, platinum group metals represent the most studied

components.¹³⁷ However, the high cost and limited availability of platinum group metals limit their application in large-scale processes. Consequently, attention has shifted to nickel, a cheaper alternative that possesses similar electronic properties and can catalyse many of the same elemental reactions performed by palladium or platinum.¹³⁸ Nickel is known for its excellent ability to form alloys with all noble metals and many transition metals, in various mass ratios. This characteristic facilitates the development of a wide range of nickel-based bimetallic systems, with compositions that can be optimized for specific catalytic applications. Recently, several studies have reported simple and effective synthesis methods for these bimetallic systems, highlighting their potential in replacing expensive noble metal-based catalysts in terms of both catalytic activity and stability.¹²⁹ Several factors influence the structure of bimetallic catalysts. Currently, a number of established methods are available for the preparation of these catalysts, either in the form of unsupported colloidal nanoparticles (NPs) or supported bimetallic NPs.¹³⁹ The choice of synthetic technique depends mainly on the desired surface structure and bulk configuration for the catalyst. For example, the co-impregnation method is widely used to produce supported bimetallic or alloy-type materials. In contrast, the sequential impregnation method is often employed to obtain materials with a core-shell structure, in which a core consisting of a less active metal (usually a 3d transition metal) is prepared first, followed by the deposition of a layer of a more active metal (often a noble metal).¹²⁹

Several wet chemical approaches have been developed for the synthesis of bimetallic nanoparticles (NPs). These can be divided into two main categories based on the mechanisms of formation: seed-mediated growth and one-pot co-reduction. Both strategies share similar fundamental principles.¹⁴⁰

In the seed-mediated growth process, metallic seeds of a relatively less active metal are initially prepared and then dispersed in a solution containing precursors of the more active metal. The controlled reduction of the second metal leads to the formation of uniform layers around the seeds, resulting in a core-shell structure.

In the one-pot co-reduction method, precursors of both metals are introduced simultaneously into the synthesis solution. In this case, the reduction potentials of the

two metals play a crucial role in determining the final architecture of the nanoparticles. Two main scenarios can occur:

1. Metals with similar reduction potentials are reduced simultaneously, forming an alloy structure.
2. Metals with different reduction potentials are reduced sequentially, resulting in a core-shell structure.

However, there is no direct relationship between the reduction kinetics and the reduction potential. The reduction kinetics also depend heavily on the synthesis conditions applied. For example, the use of surfactants, stronger reducing agents (such as NaBH_4), or high temperature solvothermal processes can induce the simultaneous reduction of metals with different reduction potentials, ultimately leading to the formation of an alloy structure.¹⁴¹

Ni-based bimetallic catalysts exhibit unique properties due to a synergistic or bifunctional effect, which distinguishes them from the starting metals. This combination offers the opportunity to design catalysts with activity and selectivity levels that exceed those achievable with monometallic nickel.

3.3 Catalyst preparation

The supported catalysts were prepared by precipitation of iron hydroxides on-to waste steel slags (SS) with a solution containing iron (II) and iron(III) salts to get a red solid (**Fe-SS**), which was in turn treated with Ni(II) solutions and subsequently calcined under dihydrogen to get the final materials (**Ni/Fe-SS** and **Ni/Fe-SSb**).

3.3.1 Synthesis and characterization of Fe-SS

Prior to coat SS with Ni catalytic centres, steel slags were treated with a $\text{Fe}^{2+}/\text{Fe}^{3+}$ (1/2 molar ratio) solution aiming at obtaining Fe_3O_4 deposited onto the inorganic material, for rendering the latter a highly magnetic support.^{142, 143} This treatment had also the scope to enhance the catalytic activity of the subsequently deposited Ni active species.¹²⁹ In fact, many studies have been reported a synergic effect between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system and another metal centre, resulting in an improving of the activity of the bimetallic catalyst compared to the monometallic one.⁸⁶ Following the precip-

itation method under alkaline conditions,¹⁴⁴ SS were mixed with a solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$, avoiding the addition of an external base, due to the strong basic features of SS. In fact, this mixing directly led to the precipitation of red iron hydroxides onto SS surface without the addition of sodium hydroxide or ammonia, which, on the contrary, was mandatory in other reported works.¹⁴⁵

In this procedure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (6.0 mmol, 1.6220 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (3.0 mmol, 0.8341 g) were dissolved in deionized water (130 mL), obtaining an orange-brown solution, which was added of SS (2.08 g) as dark grey solid. The resulting mixture was left under stirring at 35°C for 6 hours to give a colourless water phase and a reddish-brown precipitate, **Fe-SS** (Figure 26). After centrifugation (4000 rpm x 10 min), the solid was removed of the supernatant solution, washed with deionized water (3 x 3 mL) and dried overnight at 85°C.



Fig. 26 - Fe-SS matrix, steel slags were treated with a $\text{Fe}^{2+}/\text{Fe}^{3+}$ (1/2 molar ratio) solution to obtain a reddish-brown precipitate

By repeating Hammett's basicity test carried out on pristine SS, and using phenolphthalein as a pH indicator, it was noticed that the surface of the support did not turn pink as in the case of SS, but rather it remained colourless. This indicated that the surface had a $\text{pH} < 8,2$, thus more acidic than pristine SS. (Figure 27)



Fig. 27 - Hammett basicity test on the modified support Fe-SS

XRF analysis (Table 11) shows that **Fe-SS** matrix contained high quantities of Fe (38,12%w), while the amount of Ca (6,77 %w) decreased with respect to pure steel slags (31,22 %w), suggesting the replacement of calcium cations for iron ions during treatment of SS with iron salt solution to give **Fe-SS**. In fact, due to amphiphilic features of iron oxides, **Fe-SS** solution showed a slightly acid pH (around 6), which caused calcium oxide/hydroxide dissolution.

Table 11. Elemental analysis of the investigated steel slags and the Fe-SS matrix carried out by XRF analysis

Element	Steel Slag	Fe-SS
Si	3.8 ± 0.2	$2,97 \pm 0.3$
Ca	31.2 ± 1.8	$6,77 \pm 0.005$
Mn	4.7 ± 0.4	$3,87 \pm 0.08$
Fe	18.8 ± 1.4	$38,12 \pm 0.38$

XRD analyses of Fe-SS (Figure 28) revealed the presence of wustite (FeO), quartz (SiO₂), zeolite (Na(AlSi₂O₆)· H₂O), magnesite (MgCO₃), along with a significant amount of amorphous compounds, as suggested by the low level of signal/noise ratio in the diffractogram. From this XRD analysis it is possible to observe the disappearance of the signals present in the steel slags's diffractogram related to the calcium-containing minerals. This also confirms the results obtained from the XRF analyses

which prove the drastic reduction of the percentage of calcium before and after iron deposition.

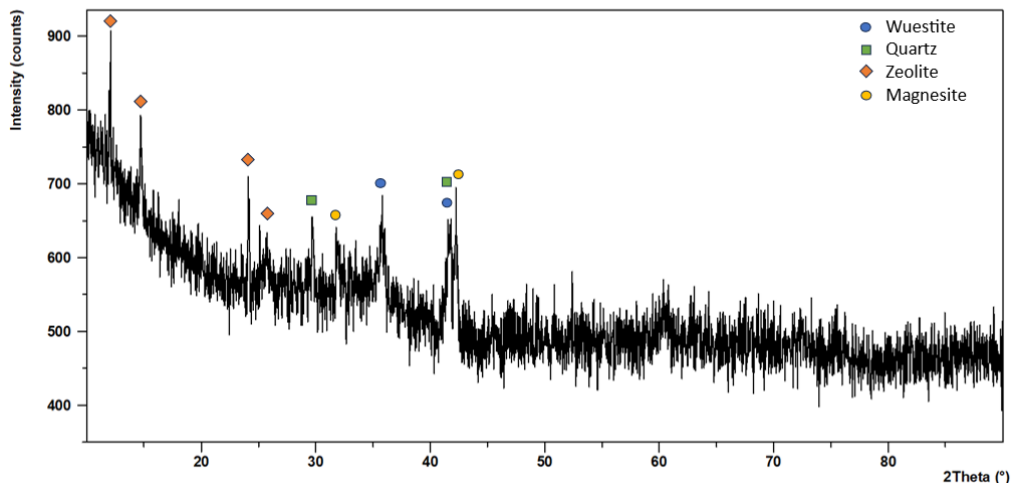


Fig. 28 - XRD diffractogram of the Fe-SS matrix

The IR spectrum (Figure 29) shows band at 3430 cm^{-1} that is due to the stretching vibration of OH functional groups. Correspondingly, the IR band at 1620 cm^{-1} is assigned to --OH bending vibrations. Peaks at 1500 and 1411 confirm the presence of carbonates,¹⁴⁶ and correspond to CO_3^{2-} asymmetric stretching vibrations. In the region of $800\text{--}1200\text{ cm}^{-1}$ corresponds to the asymmetric and symmetric stretching vibrations of Si–O bonds.^{69,147} The IR band at 970 cm^{-1} can be assigned to Si–O– stretching vibrations. The peak at 1120 cm^{-1} is attributable to the siloxane group Si–O–Si asymmetric stretching vibrations. These peaks are consistent with the presence of quartz and zeolite revealed by the XRD analysis.

The peaks at **600, 670, and 700 cm^{-1}** correspond to Fe–O stretching. [¹⁴⁸, ¹⁴⁹]

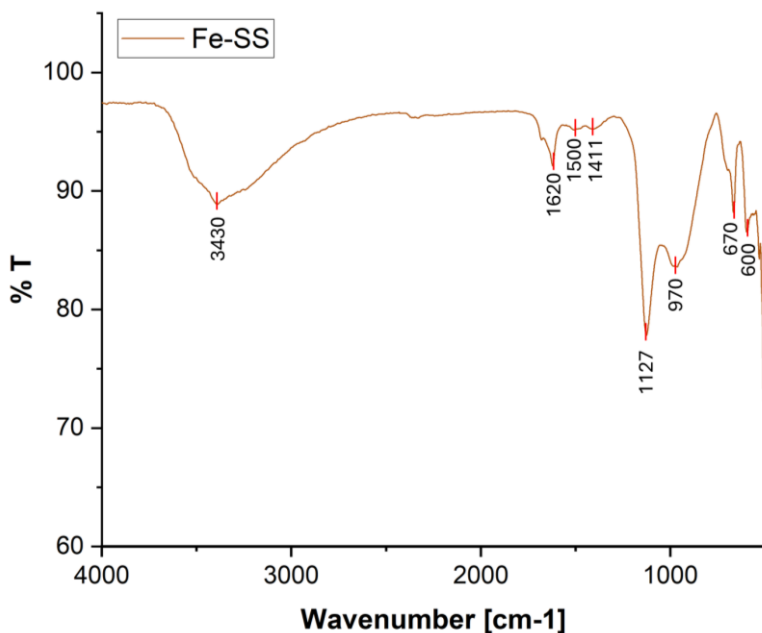
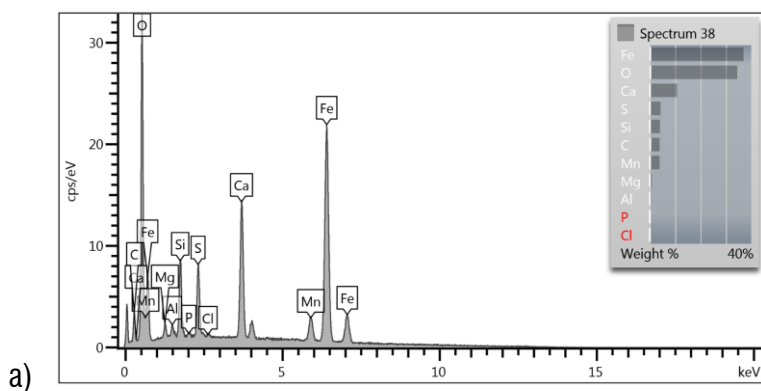


Fig. 29 - ATR-FT spectra of the Fe-SS matrix

EDX mapping (Figure 30) showed a related elemental homogeneous distribution of Fe and Si together with O. On the contrary, the distribution of Mn and Mg, which are associated with each other, was rather irregular, with their concentrations being higher in certain areas compared to others. It is observed that the distribution of sulfur in this case is correlated with that of calcium, likely due to the presence of calcium sulfate. Traces of chloride and phosphorus were also detected by EDX analysis.



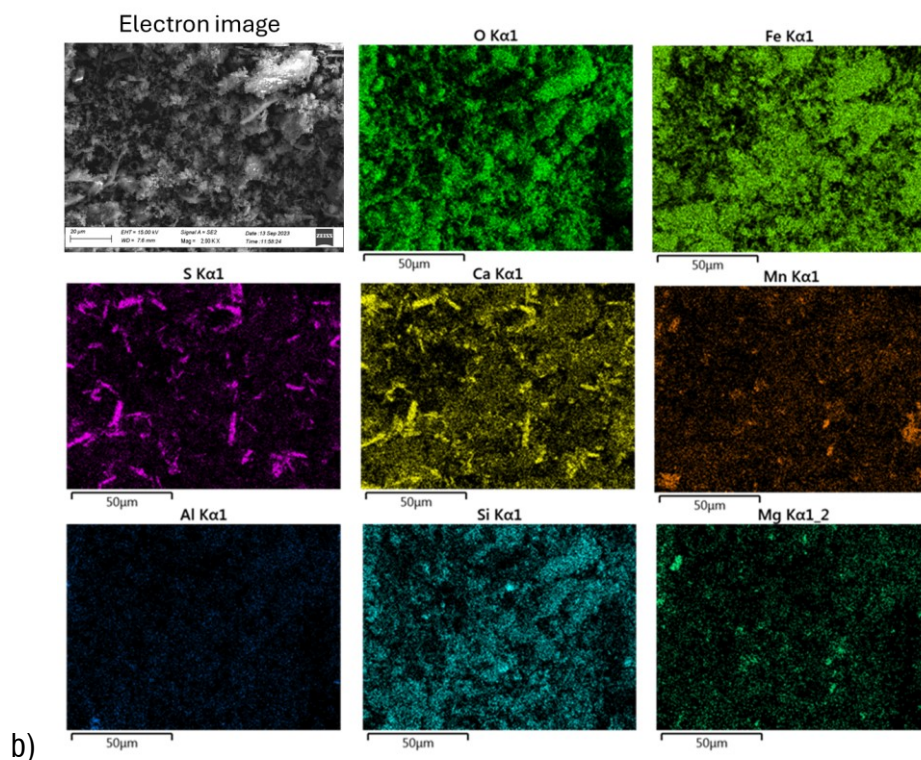
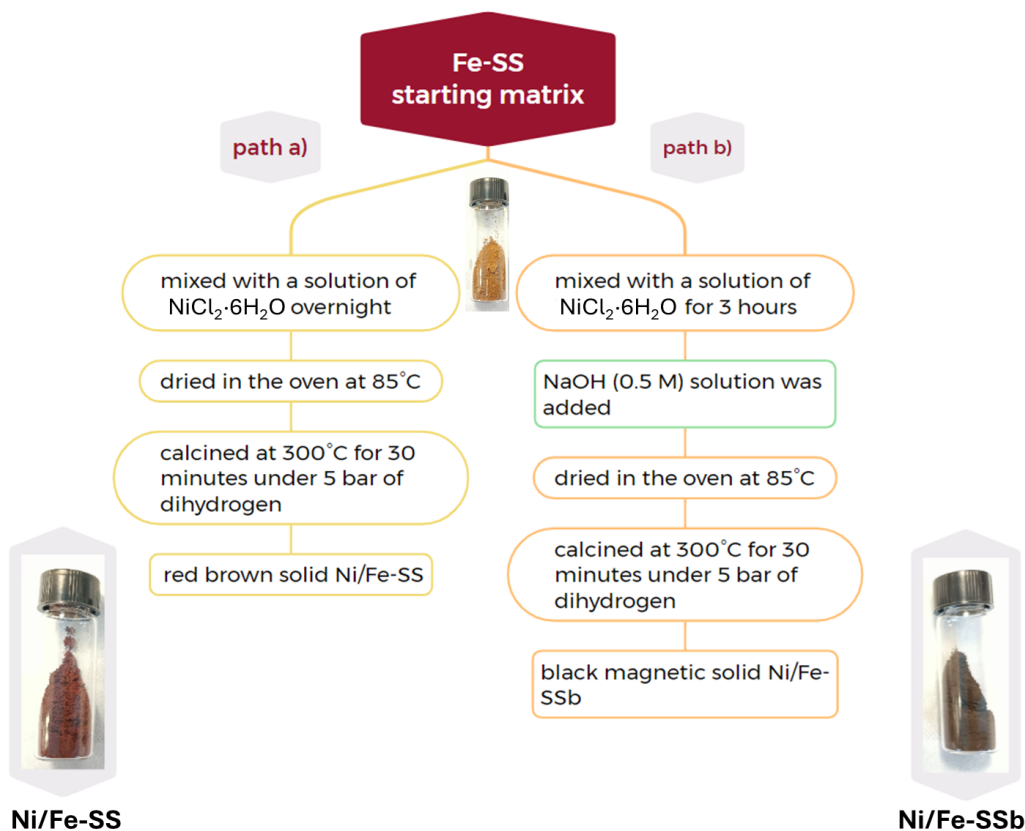


Fig. 30 – a) FESEM image and b) EDX maps of **Fe-SS**

3.3.2 Synthesis and characterization of the supported catalysts Ni/Fe-SS and Ni/Fe-SSb

The iron modified SS support, referred as **Fe-SS**, was used as starting matrix to be covered by Ni catalyst. The Ni covering procedure was carried out in two different alternative ways (path a and path b, Scheme 1):


 Scheme 2 - synthesis of **Ni/Fe-SS** and **Ni/Fe-SSb**

Path a: **Fe-SS** was mixed with a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ overnight. During this period, only a portion of the Ni^{++} cations in solution precipitated as nickel hydroxide onto **Fe-SS**, because the pH value of the supernatant water solution was not enough basic (pH value around 6) to cause its quantitative precipitation. Therefore, the whole mixture was put in an oven at 85°C and let it dry, before being calcined at 300°C for 30 minutes under an initial pressure of dihydrogen equal to 5 bar, yielding **Ni/Fe-SS** as a red brown solid.

Path b: **Fe-SS** was mixed with a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for 3 hours. Afterwards, a NaOH (0.5 M) solution was added to the mixture until the solution reached a neutral pH, causing all nickel cations in the solution to precipitate as nickel hydroxide onto **Fe-SS**. The solid was then dried in an oven at 85°C and subsequently calcined at

300°C for 30 minutes under an initial dihydrogen pressure of 5 bar, yielding **Ni/Fe-SSb** as magnetic black material.

In both cases, calcination was performed on the Fe-SS support impregnated with nickel. Calcination in a hydrogen or nitrogen atmosphere is a widely recognized method for producing metallic nanoparticles anchored to an insoluble support. This method uses thermal reduction to convert metal ions on the support into their metallic form. The heat treatment, which varies with calcination temperature, also modifies the insoluble matrix, potentially causing the loss of water, crystallization solvents molecules, or carbon-based groups. These alterations can either enhance or reduce the support's ability to stabilize and hold the resulting metal particles effectively. In this work, a temperature of 300°C was selected for performing the calcination. Qiu and coworkers found that calcination temperature is the crucial factor influencing the structure, morphology, and catalytic performance of their Ni/C catalyst. They identified in $T = 300\text{ }^{\circ}\text{C}$ the best calcination temperature for their catalyst in terms of activity,^{150,151} as found also in another reported work dealing with Ni nanoparticles supported onto a polymer matrix.³⁷

3.3.2.1. Synthesis and characterization of Ni/Fe-SS

Fe-SS (0.82 g) was added to the green solution obtained by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (3.45 mmol, 0.732 g) in 20 mL of deionized water and left under stirring at 65°C overnight. Afterwards, the whole mixture made of a light-blue water phase and a dark brown solid was put in an oven at 85°C for several hours until total water evaporation. The resulting solid (1.2614 g) was calcined at 300°C for 30 minutes under an initial dihydrogen pressure of 5 bar, yielding a slightly magnetic dark red/brown solid material (1.1579 g), referred as **Ni/Fe-SS**. (Figure 31)



Fig. 31 - Ni/Fe-SS slightly magnetic dark red/brown solid powder

XRF elemental analysis shows that **Ni/Fe-SS** contained high quantity of Ni (11%w). (Table 12)

Table 12. Elemental composition of **Ni/Fe-SS** catalyst

Element	Fe-SS	Ni/Fe-SS
Si	$2,97 \pm 0.3$	$2,06 \pm 0.07$
Ca	$6,77 \pm 0.05$	$3,75 \pm 0.05$
Mn	$3,87 \pm 0.08$	$2,18 \pm 0.02$
Fe	$38,12 \pm 0.38$	$26,42 \pm 0.54$
Ni	-	$11,24 \pm 0.78$

The diffractogram of **Ni/Fe-SS** showed the presence of three compounds (none of them containing Ni in their crystalline form: aluminium oxide hydrate $\text{AlO}(\text{OH})$, a huge amount of hematite (Fe_2O_3) and Anhydrite (CaSO_4) (Figure 32). No nickel oxide/hydroxide nor nickel metal were detected by XRD analyses, although both XRF and EDX elemental analyses confirmed the presence of Ni in **Ni/Fe-SS**.

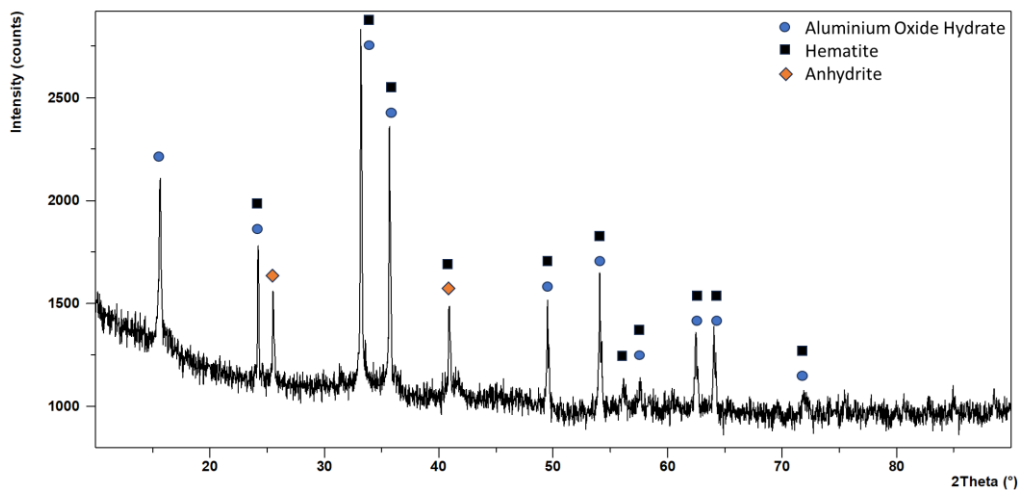


Fig. 32 - XRD diffractogram of **Ni/Fe-SS**

The FT-IR spectrum of **Ni/Fe-SS** (Figure 33) shows several distinct signals after thermal treatment.

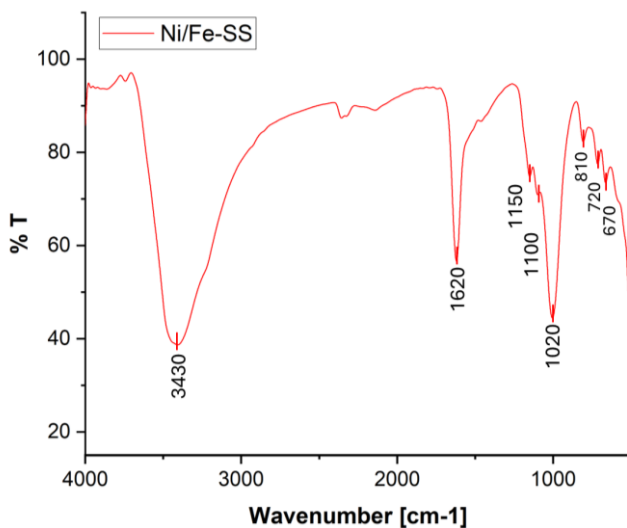


Fig. 33 – ATR-FT spectra of the catalyst **Ni/Fe-SS**

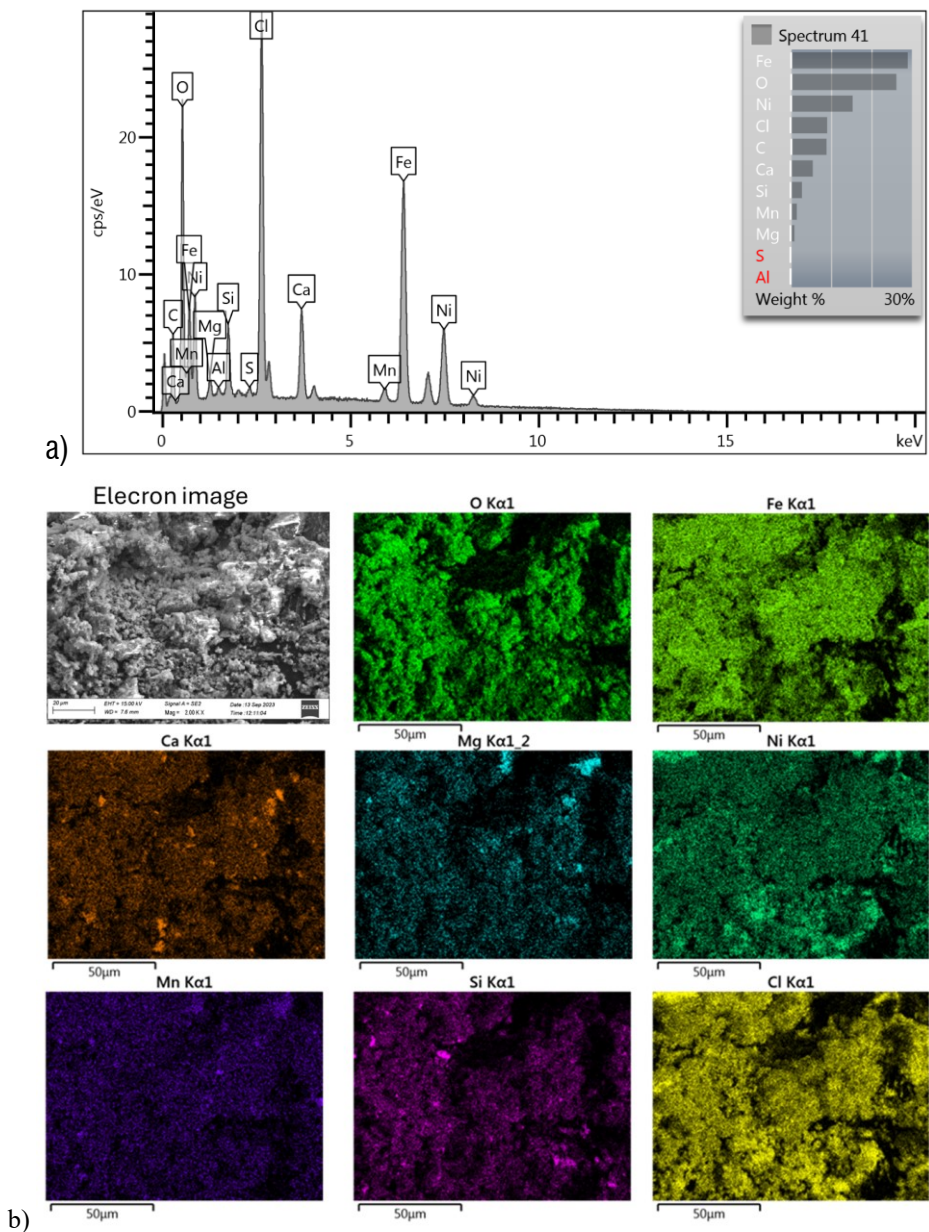
A broad band around 3430 cm^{-1} assigned to hydrogen bonded O-H stretching can be observed. This band particularly strong is due to the $\nu_{\text{asym}}(\text{Al})\text{O-H}$ and

$\nu_{\text{sym}}(\text{Al})\text{O-H}$ stretching vibration which are characteristic of metal oxy(hydroxy) compounds, such an intense signal is consistent with the presence of aluminium oxide hydrate detected by XRD analysis¹⁵²

The peak at 1620 cm^{-1} is associated with the bending vibrations of O-H feature.¹⁵³

A complex band observed between 1154 and 1000 cm^{-1} , with distinct contributions at 1150 , 1100 , and 1020 cm^{-1} , is characteristic of asymmetric Si-O-T stretching vibrations, where T represents either Si or Al.¹⁵⁴ This suggests the presence of zeolite-like or silicate-based phases in the sample. These peaks also align with the characteristic vibrations $\nu_{\text{sym}}\text{Al-O-H}$ and $\nu_{\text{asym}}\text{Al-O-H}$ modes (specifically 1155 and 1095 cm^{-1}). The signal at 810 cm^{-1} is attributed to $\nu(\text{OH})$ vibrations.¹⁵⁵ Finally, peaks at 670 , and 720 cm^{-1} are associated with Fe-O stretching vibrations, typical of iron oxides.¹⁴⁸

FESEM image (Figure 34a) of **Ni/Fe-SS** reported a porous material onto which Ni, Fe and O were homogeneously distributed (EDX maps, Figure 34b).



The TEM images of Ni/Fe-SS catalyst (Figure 35), show the formation of nanoparticles, along with irregular aggregates featuring regions of very high electron density (dark areas) and less dense regions (lighter areas). The particles appear to have variable sizes, with some regions showing distinct cubic-shaped crystals, likely due to the crystalline nature of hematite, while others exhibit a more amorphous structure.

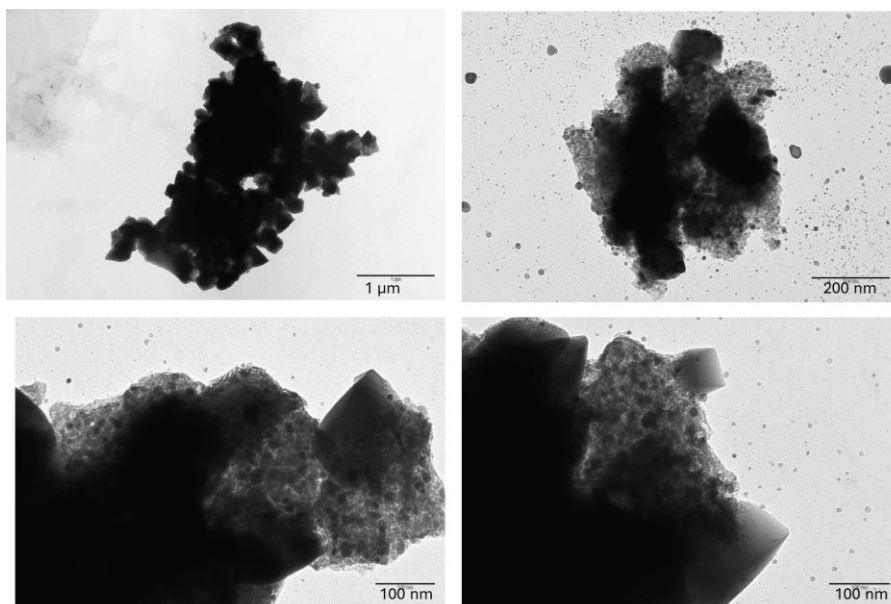


Fig. 35- TEM image of Ni/Fe-SS at different magnification after calcination

3.3.2.2. *Synthesis and characterization of Ni/Fe-SSb*

Fe-SS (0.82 g) was added to the green solution obtained by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (3.45 mmol, 0.732 g) in 20 mL of deionized water and left under stirring at 65°C for 3 hours. Afterwards, to the whole mixture, few drops of NaOH (0.5 M) solution were added until the water phase became colourless. After 1 hour stirring, the system was centrifuged, the liquid phase was removed with a glass pipette, and the solid was dried at 85°C overnight, yielding a dark grey material (1.2228 g).

0.6759 g of the dark grey material was calcined at 300°C for 30 minutes under an initial dihydrogen pressure of 5 bar, yielding a strongly magnetic black solid (0.6307 g), referred as **Ni/Fe-SSb** (Figure 36).

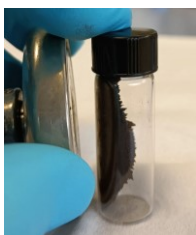


Fig. 36 - Magnetic black Ni/Fe-SSb catalyst obtained after calcination.

The black highly magnetic solid **Ni/Fe-SSb** presented almost the same elemental composition of **Ni/Fe-SS**, being Fe, Ni and Ca percent amounts equal to 26.42, 11.24 and 3.75 respectively. (Table 13)

Table 13. Elemental composition of the **Ni/Fe-SSb** catalyst.

Element	Ni/Fe-SSb
Si	1.92±0.09
Ca	4.52±0.07
Mn	2.38±0.03
Fe	22.68±0.16
Ni	13,27±0.16

The diffractogram of **Ni/Fe-SSb** (Figure 37) showed the presence of corundum (Al_2O_3), zeolite, fayalite (Fe_2SiO_4), magnetite (Fe_3O_4), that justified the magnetic properties of the material and its black colour. Hematite found in XRD spectra of **SS** and in **Ni/Fe-SS** was not detected in **Ni/Fe-SSb** diffractogram. As it happened for **Ni/Fe-SS**, no nickel oxide/hydroxide nor nickel metal were revealed by XRD analyses, although both XRF and EDX elemental analyses confirmed the presence of Ni in **Ni/Fe-SSb**.

IR spectrum (Figure 38) showed a very intense band in the range 3100-3500 cm^{-1} , due to O-H stretching of metal hydroxides, as expected because of addition of sodium hydroxide during preparation procedure. The absorption band at 1620 cm^{-1} could be attributable to O-H bending vibration mode¹⁵³ and the absorption band at 1550–1410 cm^{-1} corresponded to the asymmetric stretching vibration mode of car-

bonate anion group (CO_3^{2-}),¹⁴⁶ and peaks at 1150, 1120, 1006 cm^{-1} belonged to Si-O-Si stretching vibration.¹⁵⁴ Peaks at 870 and 800 cm^{-1} are due to O—H stretching and the peak at 560 is assigned to the Fe—O stretching mode.¹⁴⁸

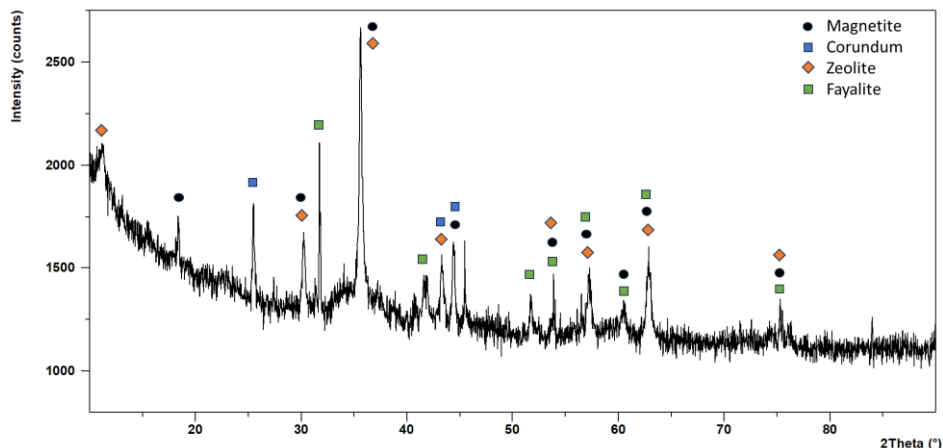


Fig. 37 - XRD diffractogram of **Ni/Fe-SSb**

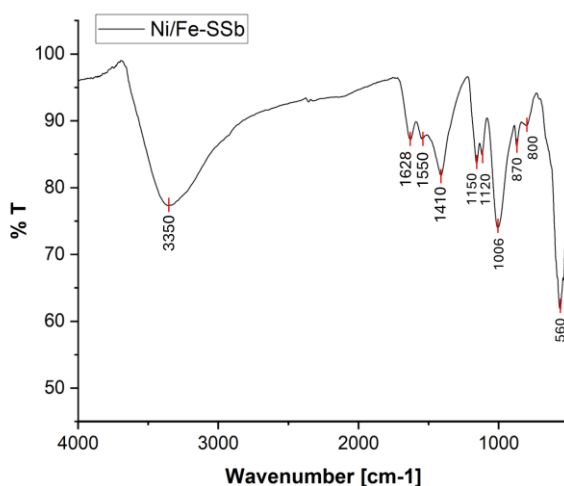


Fig. 38 - ATR-FT spectra of the catalyst **Ni/Fe-SS**

FESEM image (Figure 39a) of **Ni/Fe-SSb** reported a material composed by needles mainly composed by calcium compounds and rods onto which Ni, Fe and O were homogeneously distributed (EDX maps, Figure 39b).

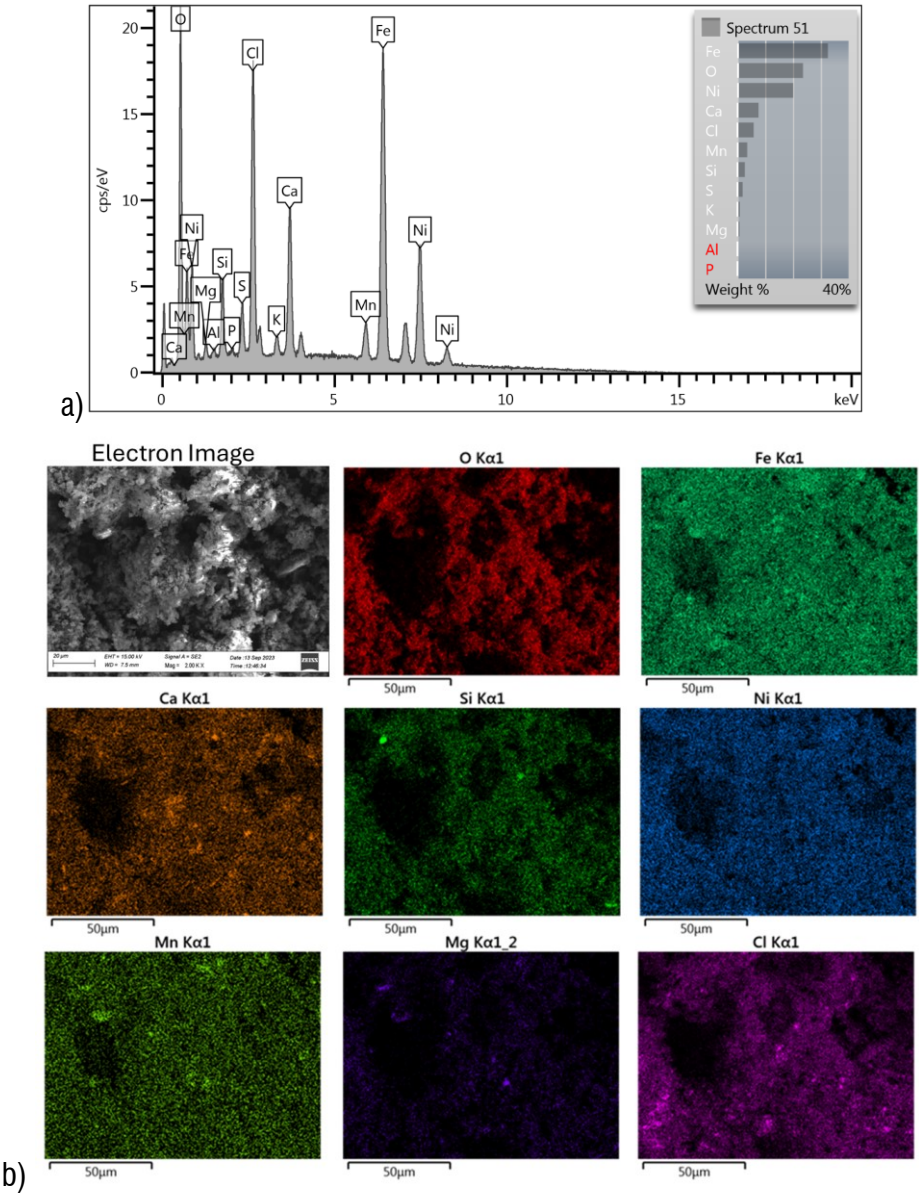


Fig. 39 -a) FESEM image and b) EDX maps of **Ni/Fe-SSb**

The TEM images of Ni/Fe-SSb (Figure 40) highlight agglomerates of particles with irregular morphologies and poorly defined edges. The particle distribution appears to be non-uniform, with denser (darker) areas that could indicate a higher concentration of Fe and Ni or metallic agglomerates.

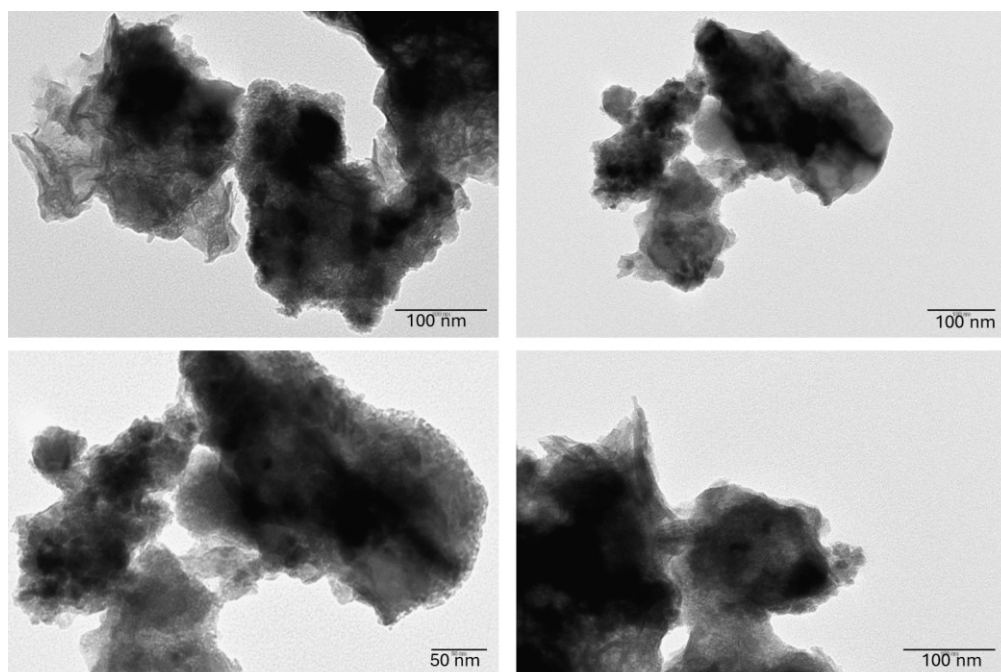


Fig. 40 - TEM image of Ni/Fe-SSb at different magnification after calcination

3.4 Upgrading of FAMES: Optimization of the reaction conditions

WCO FAMES mixture employed in the present work was constituted by methyl linoleate (C18:2, 41.9%), methyl oleate (C18:1, 48.9%), methyl stearate (C18:0, 3.2%), methyl palmitate (C16:0, 5.7%) and methyl arachidate (C20:0, 0.3%) (Figure 41). Its main biodiesel parameters were unsatisfactory, being its oxidation stability (OS) and its iodine value (IV) equal to 5.4 h and 121g/100g, respectively, thus unfitting the European thresholds (OS > 8 h; IV < 120 g/100 g). On the other hand, the cold filter plugging point (CFPP) value (-8.5°C) of the WCO FAMES mixture was pretty good, because far behind the EU limit (<10°C). These features reflected the composition of the mixture, which contained a huge amount of polyunsaturated methyl ester that caused the poor values of both OS and IV, due to its chemical instability (tendency to polymerize, oxidize, go rancidity) and the good fluidity features expressed by CFPP. To improve OS and IV parameters, it was necessary to convert all C18:2 esters

into C18.1 product by catalytic partial hydrogenation, avoiding the total saturation to methyl stearate (Scheme 2), being the latter in solid state at room temperature, thus negatively affecting fluidity parameters and CFPP value.

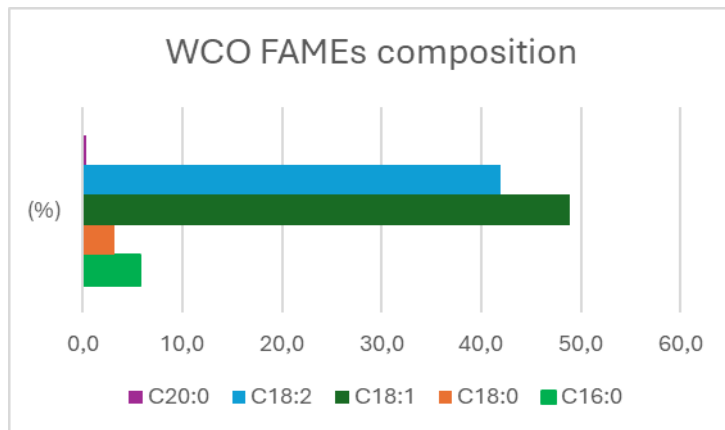
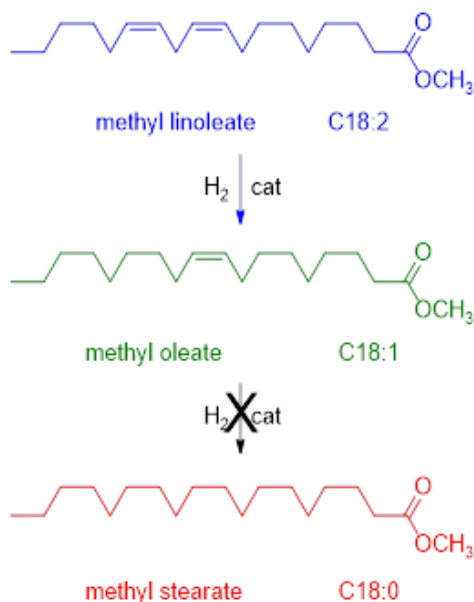


Fig. 41 - WCO FAMES composition used in the present study

In the present work, Ni/Fe-SS and Ni/Fe-SSb were employed as the catalysts for the partial hydrogenation of WCO biodiesel. Due to the amphiphilic peculiarities of Ni/Fe-SS which contained both acidic and basic sites, the catalytic tests for the optimization of reaction conditions were carried out by using Ni/Fe-SS as the catalyst. The partial hydrogenation reaction was conducted using both the conventional partial hydrogenation method, where the biodiesel hydrogenation process is carried out with molecular hydrogen (H_2) supplied in gaseous form as the reductant, and the Catalytic Transfer Hydrogenation (CTH) method, where hydrogen is supplied through sodium borohydride ($NaBH_4$), a compound acting as a hydrogen donor. The relevant results are reported in Table 14 and Table 15.



Scheme 3 - Catalytic partial hydrogenation of methyl linoleate in WCO biodiesel

3.4.1 Catalytic test: upgrading of FAMES under dihydrogen

Ni/Fe-SS (50 mg) was added to a solution of biodiesel (125 mg) in methanol (5.0 mL) in a 50 mL stainless-steel reactor. The whole mixture was placed under dihydrogen at appropriate pressures and temperatures, and left under stirring for the appropriate amount of time. The progress of the reaction was monitored by GLC and GC-MS analyses. At the end of the reaction, the catalyst was removed from the liquid phase and washed with methanol (3 x 5 mL). Then, it was dried under vacuum, weighed, and employed for subsequent catalytic runs, by using a proper amount of fresh reagent, for keeping steady the metal/substrate molar ratio. The relevant catalytic tests are summarized in Table 14. Regarding the choice of reaction conditions, the main affecting parameter using H_2 as the hydrogen source was temperature value. All researchers agree that an increase in temperature promotes the isomerization of *cis*-monounsaturated FAMES into *trans* isomers,^{112,127,132,156} as the formation of *trans* isomers is thermodynamically favoured.¹²⁰ In addition, it has been observed that high temperatures increase the conversion to fully saturated FAMES^{131,132,141} and acceler-

ate the reaction rate.^{127,132} To achieve an optimal compromise between reaction speed and selectivity toward *cis*-monounsaturated FAMES, the recommended temperature range varies between 70 to 120 °C. Another significant parameter is pressure, which influences the final products of hydrogenation. Numwong et al.¹⁴¹ showed that an increase in pressure promotes the conversion of polyunsaturated FAMES, but also increases the formation of *trans*-monounsaturated FAMES. Similar results were reported by Phumpradit et al.,¹²⁷ who found an increase in both *trans*-monounsaturated isomers and fully hydrogenated FAMES with increasing pressure. Zhu et al.,¹³² on the other hand, observed that higher pressure mainly leads to a higher reaction rate.

Table 14. Catalytic tests with Ni/Fe-SS in biodiesel hydrogenation reaction under dihydrogen.

Entry	T (°C)	t (h)	p H ₂ (bar)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP<10(°C) ^a	OS>8(h) ^a	IV<120(g/100g) ^a
0	-	-	-	3.8	44.4	51.8	-8.5	5.4	121
1	100	15	10	7.0	11.9	81.1	-4.2	13.0	89.7
2	100	10	10	6.3	15.5	78.2	-5.4	10.6	93.2
3	100	10	5	11.3	11.6	77.0	2.1	13.4	85.2
4	100	6	5	7.1	16.6	76.3	-4.3	10.1	93.3
5	100	10	2.5	6.0	26.1	67.9	-5.7	7.4	101.9
6	70	6	5	6.3	15.3	78.4	-5.4	10.7	93.0

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.

Reaction conditions: 50 mg of catalyst was added to a solution of biodiesel (125 mg) in methanol (5.0 mL) in a 50 mL stainless-steel reactor. The whole mixture was placed under dihydrogen at appropriate pressures and temperatures.

As reported in Table 14, among the various temperature and pressure conditions tested, the optimized reaction conditions were found as T=70°C, t= 6 hours, P of hydrogen = 5 bar. Under these conditions, the three parameters—CFPP, OS, and IV—fell within the limits established by European regulations (row 6, Table 14). The current biodiesel parameters of the obtained biodiesel mixtures were calculated according to equations reported in the study of Talebi et al.¹⁵⁷ who developed a user-friendly software called BiodieselAnalyzer designed to predict biodiesel parameters using the fatty acid methyl ester profile as the only input required.

3.4.2 Catalytic test: upgrading of FAMES with NaBH_4

Ni/Fe-SS (50 mg) and a suitable amount of NaBH_4 were added to a solution of biodiesel (125 mg) in methanol (5.0 mL) in a 25 mL three-necked round flask, equipped with a magnetic stirrer and a gas bubbler (Figure 42). The whole mixture was left under stirring at room temperature for the appropriate amount of time. The progress of the reaction was monitored by GLC and GC-MS analyses. At the end of the reaction, the catalyst was removed from the liquid phase and washed with methanol (3 x 5 mL). Then, it was dried under vacuum, weighed, and used for subsequent catalytic runs. The results obtained with the catalytic tests are reported in Table 15

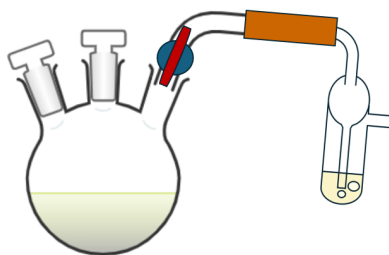


Fig. 42 - Experimental setup consisting of a three-neck round-bottom flask and a gas bubbler, used for the partial hydrogenation reaction with NaBH_4 .

Table 15. Catalytic tests with Ni/Fe-SS in biodiesel hydrogenation reaction using NaBH_4

Entry	T	t (min)	NaBH_4 (mmol)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C ^a	OS > 8h ^a	IV < 120g/100g ^a
1	RT	30	5	>99	0	0	-	-	-
2	RT	20	1.3	21.9	0.4	77.7	17.6	318.8	64.3
3	RT	20	0.8	16.0	2.1	81.9	9.1	63.8	71.2
4	RT	20	0.5	13.0	2.3	84.7	4.5	57.6	76.2
5	RT	40	0.26	9.9	10.7	79.4	0.4	14.7	82.8
6	RT	20	0.26	9.7	11.0	79.3	-0.24	14.0	85.7

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.

Reaction conditions: (50 mg) of catalyst were added to a solution of biodiesel (125 mg) in methanol (5.0 mL) with a suitable amount of NaBH_4 in a 25 mL three-necked round-bottom flask, equipped with a gas bubbler and kept under stirring at room temperature for an appropriate period.

Table 15 show that the optimal reaction conditions, which yielded satisfactory results in key parameters, CFPP, OS, and iodine value IV, were T = room temperature, t = 20 minutes, amount of sodium borohydride (NaBH_4) = 0.26 mmol. Under these conditions, the chemical reactivity is balanced, minimizing excessive hydrogenation while simultaneously reducing the percentage of polyunsaturated C18:2 chains.

3.5 Recyclability test

In the present work, studies were conducted on the reusability of the two analyzed catalysts Ni/Fe-SS and Ni/Fe-SSb, evaluating their performance through several consecutive reaction cycles. The investigation was performed considering both approaches, involving the use of both dihydrogen (H_2) and sodium borohydride (NaBH_4) as reducing agents. The results obtained, shown in Table 16-19, highlight the catalyst's sustainability in the different reaction scenarios examined.

3.5.1 Activity and recyclability test of Ni/Fe-SS

In the recyclability tests, where dihydrogen was used as the reducing agent, (Table 16) the Ni/Fe-SS catalyst produced FAME mixtures that met the limits of the three key parameters—CFPP, OS, and IV as mandated by European regulations. Starting from the third cycle, a decrease in oxidative stability below 8 hours was observed, correlating with a higher concentration of methyl linoleate in the mixture. Notably, the concentration of stearate remained constant throughout the cycles. By the fifth cycle, the resulting FAME mixture was identical to the initial one.

The last row of Table 16, describes an experimental test in which 50 mg of catalyst was used on 2.5 mmol (625 mg) of FAMES in a reaction conducted for 30 hours continuously, without performing any workup every 6 hours, followed by the addition of 125 mg of FAMES, in order to avoid possible damage to the catalyst due to intermediate treatments.

For this experiment, the same amount of catalyst used for 0.5 mmol (125 mg) of FAMES was used on a quintupled amount of substrate. When dihydrogen was used, the reaction was conducted in an autoclave at a pressure of 5 bar for 30 hours, using 2.5 mmol of FAMES. This resulted in an optimized mixture that met the limiting values of the three parameters analyzed and the oxidative stability value obtained is higher than that of the first cycle.

When sodium borohydride (NaBH_4) was used as the reducing agent, (Table 17) the limits for the three parameters were maintained up to the third cycle. In the fourth and fifth cycles, the concentration of FAMES remained relatively stable, with only the oxidative stability parameter falling slightly below the regulatory threshold. Again, an experimental test was conducted where the five cycles of the reaction were carried out continuously without performing any workup between cycles. The continuous reaction was carried out in a three-neck flask, loading 50 mg of catalyst, 10 mL of MeOH and 2.5 mmol of FAMES. During the process, 0.26 mg of NaBH_4 was added every 10 min, allowing the 5 consecutive cycles to be completed without the need for workup. The resulting final mixture showed a significant increase in C18:1 and a drastic reduction in C18:2, with OS and IV parameters conforming to regulatory limits. In addition, the resulting C18:0 content ensures a CFPP of less than 10.

Table 16. Recyclability tests using dihydrogen as the reducing agent and Ni/Fe-SS as catalyst

Run	T (°C)	t (h)	p H ₂ (bar)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C ^a	OS > 8h ^a	IV < 120g/100g ^a
1st	70	6	5	6.3	15.3	78.4	-5.4	10.7	93.0
2nd	70	6	5	7.7	11.2	81.2	-3.3	13.8	87.6
3rd	70	6	5	6.8	28.1	65.1	-4.7	7.0	103.6
4th	70	6	5	5.8	37.7	56.5	-6.1	5.9	112.3
5th	70	6	5	4.8	44.3	50.9	-7.1	5.5	116.4

1st-bis^b	70	30	5	12.0	6.5	81.5	3.2	21.9	79.8
[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations. [b] - experimental test in which 50 mg of catalyst was used on 2.5 mmol (625 mg) of FAMES in a reaction conducted for 30 hours continuously. Reaction conditions: The reaction was carried out at 5 bar of dihydrogen pressure and 70°C for 6 hours, starting from 625 mg of FAMES and 250 mg of catalyst. The metal/substrate molar ratio was maintained constant throughout all cycles.									

Table 17. Recyclability tests using NaBH₄ as the reducing agent and Ni/Fe-SS as catalyst

Run	T (°C)	t (min)	NaBH ₄ (mmol)	C18:0 (% _w)	C18:2 (% _w)	C18:1 (% _w)	CFPP<10°C ^a	OS>8h ^a	IV<120g/100g ^a
1 st	RT	20	0.26	9.7	11.0	79.3	-0.24	14.0	85.7
2 nd	RT	20	0.26	12.6	15.6	71.9	4.3	10.9	84.4
3 rd	RT	20	0.26	12.8	22.7	64.4	4.8	8.3	89.7
4 th	RT	20	0.26	16.4	26.8	56.8	9.8	7.5	90.0
5 th	RT	20	0.26	15.1	28.5	56.4	8.0	7.2	91.6
1 st -bis ^b	RT	50	1.3	16.1	6.1	77.8	9.3	23.8	73.9
[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations. [b] - experimental test in which 50 mg of catalyst was used on 2.5 mmol (625 mg) of FAMES in a reaction conducted for 50 minutes continuously. Reaction conditions: The reaction was carried out at room temperature for 20 minutes, in 10 mL of MeOH starting from 250 mg of FAMES and 100 mg of catalyst. The metal/substrate molar ratio was maintained constant throughout all cycles.									

3.5.2 Activity and recyclability tests on Ni/Fe-SSb

The **Ni/Fe-SSb** magnetic catalyst showed a different behavior than Ni/Fe-SS. When dihydrogen was used as the reducing agent (Table 18), the first cycle showed a slight catalytic activity, even though the final FAMES mixture was almost identical to the initial one. The percentage of C18:1 remained constant compared to the initial FAMES mixture, while C18:2 decreased slightly, accompanied by an increase in C18:0. However, as early as the second cycle, the mixture of FAMES was almost identical to the starting mixture, showing an almost complete loss of catalytic activity of the catalyst.

When NaBH_4 was used as the reducing agent (Table 19), the catalytic activity was more intense, and only the first cycle resulted in values of OS, IV, and CFPP falling within the limits set by European regulations.

However, during the second and third cycles, the final mixtures were similar to each other, and the catalyst showed a slight catalytic activity; in fact, the percentage of optimized FAMES was comparable to the initial one.

Table 18. Recyclability tests using dihydrogen as the reducing agent and Ni/Fe-SSb as catalyst

Run	T (°C)	t (h)	p H ₂ (bar)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C ^a	OS > 8h ^a	IV < 120g/100g ^a
1st	70	6	5	7,52	39,04	53,43	-3,08	5,87	109,25
2nd	70	6	5	3.9	43.0	53.2	-8.5	5.6	116.3
3rd	70	6	5	4.1	46.8	49.0	-8.5	5.3	121.1

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.
Reaction conditions: The reaction was carried out at 5 bar of dihydrogen pressure and 70°C for 6 hours, starting from 625 mg of FAMES and 250 mg of catalyst. The metal/substrate molar ratio was maintained constant throughout all cycles.

Table 19. Recyclability tests using NaBH_4 as the reducing agent and Ni/Fe-SSb as catalyst

Run	T (°C)	t (min)	NaBH ₄ (mmol)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C ^a	OS > 8h ^a	IV < 120g/100g ^a
1nd	RT	20	0.26	13.5	17.0	69.6	5.6	10.2	84.8
2rd	RT	20	0.26	10.2	36.7	53.2	1.0	6.1	103.5
3th	RT	20	0.26	10.3	37.5	52.3	1.3	6.0	106.5

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.
Reaction conditions: The reaction was carried out at room temperature for 20 minutes, in 10 mL of MeOH starting from 250 mg of FAMES and 100 mg of catalyst. The metal/substrate molar ratio was maintained constant throughout all cycles.

3.6 Final consideration

The data analyses reported suggest that the two different synthesis procedures led to the formation of distinct catalysts with different catalytic activities, both containing iron and nickel species. In the absence of sodium hydroxide (Scheme 1a), the red-brown solid obtained prior to calcination contained Ni(II) species impregnated on the surface of Fe-SS after water evaporation. During calcination at 300°C under hydrogen, some of the Ni(II) centers were presumably reduced to metallic nickel (oxidation state zero).

Several studies have reported the reduction of solid Ni(OH)_2 , NiO , and even NiCl_2 to nickel nanoparticles (NPs) under H_2 at various temperatures.^{158, 159} In any case, it has been observed that the reduction of Ni(II) to Ni NPs under H_2 is favored by increasing both the temperature and calcination time^{160, 161} and by using a solid support that promotes nucleation.¹⁶² Furthermore, the presence of Fe(II) has been reported as beneficial for the reduction of Ni(II), as Fe(II) is oxidizable to Fe(III).¹⁶³

Although Fe(II) species were added to the SS support during the synthesis process, they were never detected via XRD analysis of Ni/Fe-SS, likely due to their oxidation. Therefore, the red-brown color of Ni/Fe-SS could be attributed to the presence of $\alpha\text{-Fe}_2\text{O}_3$ (XRD analysis, Figure 32).

What emerges from the results of the catalytic tests is that the Ni/Fe-SSb catalyst exhibited much lower catalytic activity compared to the Ni/Fe-SS catalyst, despite both of them have the same elemental composition, as demonstrated by EDX and XRF analyses, and supporting almost similar compounds, as evidenced by XRD diffractograms (Figures 32 and 37). The main difference between the two catalysts lies in the nature of the iron oxides present: magnetite (Fe_3O_4) is found in Ni/Fe-SSb, while hematite ($\alpha\text{-Fe}_2\text{O}_3$) is present in Ni/Fe-SS. This result aligns with the literature: the formation of magnetite from an Fe(II)/Fe(III) system under alkaline and anaerobic conditions has been well known since 1992. On the contrary, the absence of alkaline conditions during the synthesis of Ni/Fe-SS led to the formation of $\alpha\text{-Fe}_2\text{O}_3$.^{164, 165}

To investigate potential further differences between the two catalysts, the Hammett test was conducted on both materials, initially using phenolphthalein as the

indicator. Applying a few drops of the indicator solution onto the catalysts, no color change or transition to pink was observed, a phenomenon that instead occurs in the case of the pristine SS support (Figure 43a). This result indicates that both catalysts have a more acidic surface compared to the SS support, with a pH lower than 8.2.

To gain additional insights, a new indicator more suitable for detecting pH variations in a more acidic range was selected. A mixture of methyl red and bromocresol blue was used, which assumes different colors depending on the pH: orange at $\text{pH} < 4.6$, lavender blue at approximately pH 5, and bright green at $\text{pH} > 5.2$.¹⁶⁶ Repeating the Hammett test with this new indicator, the results (Figure 43b) showed that the Ni/Fe-SS catalyst produced an orange coloration ($\text{pH} < 4.6$), while Ni/Fe-SSb resulted in a dark green coloration ($\text{pH} > 5.2$, but < 8.2 as revealed by the phenolphthalein test). The SS support as a reference exhibited a bright green color ($\text{pH} > 8.2$ as revealed by the phenolphthalein test).

These results suggest that the surface of the Ni/Fe-SSb catalyst is more basic compared to that of the Ni/Fe-SS catalyst. This difference in surface properties could significantly affect the catalytic activity of both materials.

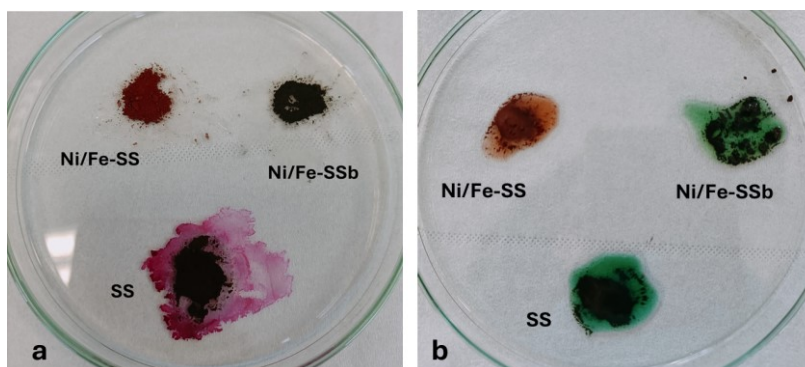


Fig. 43 - Hammett test results for Ni/Fe-SS, Ni/Fe-SSb, and SS. (a) Using phenolphthalein as an indicator, (b) with a methyl red and bromocresol blue mixture.

Furthermore, it has been reported in the literature that a parameter that plays an important role in both the activity and the selectivity of the catalytic system, influ-

encing the interaction between unsaturated FAMES and the catalyst surface, is the acidity of the solid surface. Therefore, catalysts with a more acidic nature have shown higher activity than neutral or basic ones. In a specific study,⁸⁵ the use of steel slag as a support for nickel nanoparticles was investigated, showing that the best catalytic effect in catalytic reforming of pine wood pyrolysis volatiles was obtained when the support was activated by an acidification process. Specifically, steel slag activated with a nitric acid solution at a concentration of 0.5 mol/L showed optimal performance. This treatment resulted in a tar conversion rate of 97.61%, an increase of 21.24% over untreated conditions. In the same study, the synergistic effect between the iron in the support and nickel was also investigated. This interaction promoted the formation of active centers, such as Ni-Fe alloys and catalytically relevant compounds, further improving the reaction efficiency and the ability of the catalyst to resist coke deposition. These results underscore the crucial role of both the chemical activation of the support and the synergy between the metals. Another study was conducted on the effect of acidity of Pd catalysts supported on nanoporous carbons derived from cattail flower biomass (CTF) in the partial hydrogenation reaction of fatty acid methyl esters.¹⁶⁷ Two types of carbon supports chemically activated with KOH (basic) and H_3PO_4 (acidic) were analyzed (respectively named Pd/NPC-K and Pd/NPC-H). The results showed that the acidity of the support significantly improved the efficiency of the partial hydrogenation reaction by facilitating greater accessibility of FAME molecules to the active sites of the catalyst, increasing the selectivity toward the desired product (C18:1) and accelerating the initial rate of the reaction. It was observed that the Pd/NPC-H catalyst could achieve a 90% conversion of poly-FAME at 45 minutes, while the Pd/NPC-K catalyst required a longer time to reach the same conversion rate of poly-FAME components. The higher acidity also helped to limit the complete hydrogenation to C18:0, maintaining a high level of mono-FAME (C18:1) and thus ensuring greater oxidative stability of the final product. Indeed, it has been observed that the electron-rich double bonds of poly-FAME molecules tend to preferentially adsorb on acidic surfaces, thus improving the efficiency of the hydrogenation reaction. This behavior has been reported in the literature.^{122,125,168,169} In a study on

partial hydrogenation of FAMES, where the use of catalysts with the same palladium loading (0.5wt%) but different acidity of support led to different results. The catalyst with less acidic support gave low conversion of polyunsaturated FAMES.¹⁶⁸

The catalyst with weak acidity showed the best selectivity toward cis-monounsaturated FAMES. Increasing the acidity of the support reduced the overall selectivity. In a further study, the influence of alkaline and alkaline-earth salts on the catalytic performance of Pd/SiO₂ in the partial hydrogenation of FAME derived from soybean oil was investigated.¹⁶⁸ It was found that Pd-Ba/SiO₂ showed the highest catalytic activity (highest TOF) due to the low density of basic sites, while Pd-Na/SiO₂, with the highest density of basic sites, performed the worst results due to limited interaction between the active sites and the FAME molecules.

Further analysis on the acidity of the support can be done by repeating the same Hammett test on the Ni/Fe-SS catalyst after the first and fifth reaction cycles using a methyl red and bromocresol blue mixture. (Figure 44)

The results show a progressive loss of acidity of the Ni/Fe-SS catalyst from the first to the fifth reaction cycle. This phenomenon is likely related to the reduction in catalytic activity observed between subsequent cycles, suggesting that surface acidity plays a key role in maintaining catalytic performance over time.

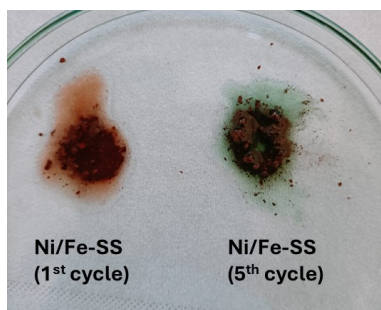


Fig. 44 - Hammett test results on the Ni/Fe-SS catalyst after the first and fifth reaction cycles using a methyl red and bromocresol blue mixture.

To demonstrate the synergy between iron and nickel in the bimetallic configuration of the Ni/Fe-SS catalyst, and to better understand the individual contributions of

each component within the investigated catalytic system, the catalytic activity of three reference catalysts was compared. In these reference systems, one of the key components—iron, nickel, or the steel slag (SS) support—was alternatively omitted.

The three resulting catalysts were:

- Fe-SS: Iron deposited on the steel slag support, with nickel absent.
- Ni-SS: Nickel deposited on the steel slag support, without iron.
- Ni-MC: Nickel supported on commercial magnetite, without SS as support.

This comparative approach allows an investigation into the role of each component. The absence of a specific element in each catalyst highlights its individual impact on the catalytic performance, providing valuable insights into the cooperative effects observed in the fully integrated Ni/Fe-SS system. The inclusion of Ni-MC, a commercially available nickel catalyst on magnetite, serves as an additional point of reference to evaluate the influence of the SS support and its interaction with the active metals.

The Ni-SS catalyst and the Ni-MC catalyst was synthesized following the same procedure used for the Ni/Fe-SS catalyst, with the only difference being that the support used for Nickel is unmodified SS or commercial magnetite instead of Fe-SS. The partial hydrogenation reaction was carried out using the two different reducing agents used in this work, molecular hydrogen and NaBH_4 .

When dihydrogen was used as a reducing agent (Table 20), none of the three cases produced mixtures with adequate oxidative stability, being the values obtained below the threshold established by European standards. This result was observed despite the use of more stringent experimental conditions—such as higher temperature, prolonged reaction time and higher hydrogen pressure—than those used with the Ni/Fe-SS catalyst. Even when NaBH_4 was used as the reducing agent (Table 21), neither Ni-SS nor Ni-MC catalysts were active but exhibited lower catalytic activity compared to Ni/Fe-SS catalyst combined to lower selectivity towards C18:1 product. This demonstrates how the nature of the support is highly relevant in determining the catalytic activity of the catalyst. It also confirms, as previously mentioned, that the synergy between the two metals plays a significant role. The catalyst that did not contain

nickel, Fe-SS, was slightly catalytically active under dihydrogen (Table 20), and totally inactive in the presence of NaBH_4 (Table 21).

Table 20. Catalytic performance of Fe-SS, Ni-SS, and Ni-MC catalysts using dihydrogen as the reducing agent.

Cat.	T (°C)	t (h)	H ₂ (bar)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C	OS > 8h ^a	IV < 120g/100g ^a
Fe-SS	100	10	10	4,4	31,8	63,8	-8,5	6,4	111,2
Ni-SS	100	10	10	8,2	25,8	66,0	-2,56	7,4	95,2
Ni-MC	100	10	10	2,1	40,2	57,7	-12.23	5.6	114.6

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.
Reaction conditions: 50 mg of catalyst was added to a solution of biodiesel (125 mg) in methanol (5.0 mL) in a 50 mL stainless-steel reactor. The reaction was carried out under stirring at 10 bar of dihydrogen pressure at 100°C for 10 hours.

Table 21. Catalytic performance of Fe-SS, Ni-SS, and Ni-MC catalysts using NaBH_4 as the reducing agent.

Cat	T (°C)	t (min)	NaBH ₄ (mmol)	C18:0 (%wt)	C18:2 (%wt)	C18:1 (%wt)	CFPP < 10°C	OS > 8h ^a	IV < 120g/100g
Fe-SS	RT	20	0.26	5.0	46.0	49.0	-6.6	5.2	116.4
Ni-SS	RT	20	0.8	16.7	22.8	60.5	10.2	8.2	88.1
Ni-MC	RT	20	0.8	9.5	27.9	62.5	-0.4	7	101.1

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.
Reaction conditions: 50 mg of catalyst were added to a solution of biodiesel (125 mg) in methanol (5.0 mL) with a suitable amount of NaBH_4 in a 25 mL three-necked round-bottom flask, equipped with a gas bubbler and kept under stirring at room temperature for 20 minutes.

3.7 Conclusions

In this work, the combination of the intrinsic chemical properties of steel slag and the properties of the metals Fe and Ni allowed the synthesis of two bimetallic catalytic systems (Ni/Fe-SS and Ni/Fe-SSb) that showed synergy between the two metals. Iron acted as a promoter, enhancing the efficiency of nickel active catalytic sites. This cooperation between the two metals resulted in a high degree of selectivity toward C18:1, minimizing over-hydrogenation toward C18:0 and optimizing the overall qualities of the mixture of FAMES.

This work also highlighted the crucial role played by the surface acidity of the catalyst support in maintaining both catalytic activity and selectivity over reaction cycles. In this context, Hammett's tests observed a clear difference in surface acidity between Ni/Fe-SS and Ni/Fe-SSb catalysts, with a direct impact on their catalytic performance. In particular, a more acidic surface found for the Ni/Fe-SS catalyst was found to provide better interaction between unsaturated substrates and catalyst active sites, thus improving the efficiency of partial hydrogenation reactions. Recyclability tests revealed a progressive loss of catalyst surface acidity after multiple cycles of use, a phenomenon that appears to go hand in hand with the observed reduction in catalytic activity. This concurrence suggests a possible correlation between the two aspects.

In conclusion, this work represents further exploration in the field of waste valorization through its transformation into efficient and sustainable catalysts, offering a promising approach for the upgrading of biodiesel obtained from WCO.

3.8 Material and Methods

All chemicals and solvents were purchased from commercial sources and used as received. Tap water was deionized before use by ionic exchange resins (Millipore). Waste cooking oil (WCO) was obtained from domestic waste. FAMES were prepared from WCO through a transesterification reaction according to the procedure reported by Fiore et al. (2020).³⁷ Monitoring of the reactions was carried out using gas chromatography (GC) technique. Gas chromatography-mass spectrometry (GC-MS)

data (EI, 70 eV) were acquired on a HP 6890 instrument using an HP-5MS cross-linked 5% phenyl methyl siloxane (30.0 m x 0.25 mm x 0.25 mm) capillary column coupled with a HP 5973 mass spectrometer. The products were identified by comparing their GC-MS characteristics with those of the pure samples. Gas chromatography analyses were carried out using an HP 6890 instrument equipped with a flame ionization detector (FID) and a capillary column coated with a cyanopropyl stationary phase (DB-FastFAME, 90 m x 0.25 mm x 0.25 μ m). Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FT/IR 4200 spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen flow (40 mL min⁻¹) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 700 °C with a heating rate of 10 °C min⁻¹. Surface morphology was investigated on a selected piece of sample considered to be representative of the material. A FESEM Zeiss Sigma 300 VP (Zeiss Oberkochen, Germany) equipped with an energy dispersive spectrometer (EDS) C-MaxN SDD (Oxford Instruments, Oxford, U.K.) with an active area of 20 mm² (Oxford Instruments, Oxford, U.K.) was used to perform analysis on the selected samples. The EDS spectrometer was calibrated using MAC standards (Micro-Analysis Consultants Ltd., United Kingdom) for elemental analysis.

X-ray powder diffraction data were collected in air using a PANalytical Empyrean X-ray diffractometer with Bragg-Brentano geometry, large beta filter-Nickel, detector (PIXcel3D) and CuK α radiation, operating at 40 kV/40 mA. The X-ray data were collected in the 2 θ range 10–90° (step size 0.026, Scan Step Time 996.54 s). The diffraction patterns were processed using the PANalytical B.V. software HIGHScore Plus version 3.0e. To determine the crystallite size of the identified phases, a LeBail analysis was performed using Profex version 3.5.0

Rietveld refinement,^{82,170} is a computational technique widely used in crystallography to extract detailed structural information from powder diffraction data. By iteratively optimizing a calculated diffraction pattern to align with experimental data, this method refines instrumental and crystallographic parameters, yielding a precise structural model.¹⁷⁰

In this study, Rietveld analysis was conducted using Profex software (v. 5.3.0), which provides a graphical interface for the BGMN refinement program (*Döbelin & Kleeberg, 2015*). The refinement process involved the optimization of parameters such as scale factors, cell parameters, crystallite size distribution, microstrain, preferential orientation, and thermal parameters. Initial parameter values were sourced from crystallographic databases.

Peak profile modeling utilized a Lorentzian function to represent the diffraction peaks, incorporating three primary contributions:

1. Instrumental Function (G): Describes the contribution of instrumental factors to peak broadening.
2. Sample Function (P): Accounts for broadening caused by crystallite size and microstrain.
3. Wavelength Distribution Function (D): Reflects the spread of the X-ray wavelength used during the experiment.

The iterative refinement adjusted these parameters through numerical optimization, specifically employing least-squares minimization to minimize discrepancies between the experimental and calculated diffraction patterns. This approach allowed for the accurate separation of peak broadening effects, in order to derive an accurate quantification of crystallite size of the occurred crystal phases.

The quality of the fit was evaluated using statistical indicators such as the weighted Rietveld factor (Rwp) and reduced chi-squared (χ^2). The final output included refined structural parameters and precise quantitative estimates of crystallite sizes.

Transmission electron microscopy (TEM) images were obtained using Philips EM 430 microscope (TEM) operating at 300 kV.

CHAPTER IV

SYNTHESIS OF CELLULOSE ACETATE-BASED CATALYSTS FOR THE BIODIESEL UPGRADING REAC- TION

4 SYNTHESIS OF CELLULOSE ACETATE-BASED CATALYSTS FOR THE BIODIESEL UPGRADING REACTION

4.1 Introduction

In this work, a waste material of environmental significance, cigarette butts, was studied as a support for Ni⁰ nanoparticles intended for the synthesis of catalysts for the biodiesel upgrading reaction. This approach aims to enhance a highly polluting waste by transforming it into a functional and sustainable material for applications in heterogeneous catalysis. There are an estimated 967 million smokers worldwide, and approximately 6 trillion cigarettes are produced annually.¹⁷¹ Cigarettes are composed of a cellulose acetate filter, tobacco, and wrapping paper. These filters are designed to retain harmful substances in cigarette smoke.¹⁷² Improper disposal of cigarette butts (CBs) is a common problem, as smokers often discard them randomly into the environment. CBs are the most common type of litter worldwide and it is essential to find alternative ways to repurpose this waste, transforming it into a high-value-added product. The main objective of the research is to obtain a cellulose acetate fiber clean of major pollutants from cigarette smoke, to serve as a stable support for metal particles that constitute the catalytically active component of the catalyst. To achieve this, it was necessary to develop and optimize cleaning methods that were not only effective but also environmentally friendly, in line with the principles of green chemistry.

The filter cleaning step was carried out using different types of deep eutectic solvents (DES), a class of alternative solvents known for their sustainability and versatility. After testing and selecting the most effective DES, the cleaned cellulose acetate fibers were used as a support for the synthesis of the new catalyst. This process made it possible to combine waste valorization with the production of high-performance materials, contributing both to the reduction of the environmental impact

of cigarette filters and to the development of innovative catalysts for sustainable energy applications.

4.2 Cellulose acetate

Cellulose is considered the most abundant and widespread organic compound on Earth, forming a fundamental natural resource for the plant kingdom. It constitutes the supporting structure of the cell walls in green plants, providing strength and stability to each plant cell.¹⁷³ Cellulose, indeed, plays a crucial role in maintaining the structure and stability of plants, aiding in preserving their shape and rigidity. This natural polymer is also readily available resources on the planet. From a chemical perspective, cellulose is a linear homopolysaccharide, composed of numerous β -D-glucopyranose units, connected by β -1,4-glycosidic bonds (Figure 45a). This bonding confers substantial structural resistance to cellulose. Each year, global cellulose production is estimated at approximately 7×10^{10} tonnes, an extraordinary quantity that can be derived from a range of natural sources such as wood, plants, algae, tunicates, and certain types of bacteria.¹⁷⁴ Cellulose acetate is a derivative form of cellulose, in which mainly the 6- followed by the 3- and 2- hydroxyl groups of cellulose¹⁷⁵ are replaced by acetate groups ($-\text{OCOCH}_3$) through an acetylation reaction (Figure 45b), but also the remaining OH could be acetylated under specific conditions.

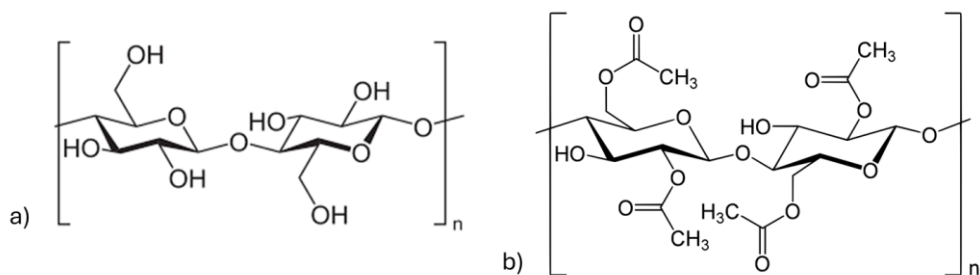


Fig. 45 - Structure of cellulose (a) and cellulose acetate (b)

The synthesis of cellulose acetate (CA) involves replacing hydroxyl groups in cellobiose with acetyl groups, using acetic anhydride and acetic acid, with sulfuric

acid acting as a catalyst.¹⁷⁶ Early research on the acetylation of cellulose dates to approximately 1865, credited to Schutzenberger.¹⁷⁷ Cellulose acetate is an ester recognized for its excellent physical characteristics and is mainly used to produce membranes, films, fibers, filters, and as a component in adhesives and pharmaceuticals.¹⁷⁸ CA fibers exhibit a high modulus of elasticity, remarkable tensile strength, and notable flexibility, making them well-suited for various industrial and biomedical applications.¹⁷⁹ Cellulose acetate has commercial interest because it can be produced from recycled sources, such as bean straw,¹⁸⁰ mango seeds,¹⁸¹ and it can be recycled and repurposed from waste materials such as cigarette butts. Current studies highlight that DS, defined as the average number of acetyl groups replacing hydroxyl groups per glucose unit, significantly influences the solubility and mechanical properties of CA.¹⁸² The degree of acetyl substitution in cellulose is determined by the specific experimental parameters employed.¹⁸³ The maximum DS is achieved when all hydroxyl groups are replaced by acetyl groups, resulting in a value of three. Typically, cellulose is initially converted into cellulose triacetate, also referred to as primary cellulose acetate, which is subsequently hydrolyzed to produce cellulose acetates with lower degrees of esterification.¹⁸⁴ The most prevalent form of cellulose acetate fiber features an acetate group on approximately 2–2.5 of every three hydroxyl groups. This form, known as cellulose diacetate, is referred to as secondary acetate or simply as "acetate." Replacing the hydroxyl groups in cellulose with acetyl groups enhances its solubility and modifies its chemical, thermal, mechanical, and physical properties.¹⁸⁵ A higher DS results in a polymer that is more soluble in solvents like THF and acetone, whereas cellulose (DS = 0) remains insoluble in most conventional solvents.¹⁸⁶ An increase in DS results in a polymer that becomes more soluble in solvents such as acetone and tetrahydrofuran (THF). It is well-established that cellulose (DS = 0) is insoluble in most conventional solvents (Kono et al., 2015). Cellulose diacetate dissolves in acetone or THF, while cellulose triacetate is soluble in dichloromethane and other chlorinated solvents.¹⁸⁷ Depending on its processing, cellulose acetate can be used for different applications. Films were made from cellulose triacetate, membranes and fibers from cellulose 2–2.5-acetate.¹⁸⁸ The low toxicity and biodegradability of CA

make it suitable for numerous applications in medicine and biotechnology, such as controlled drug delivery systems.¹⁸⁹

4.2.1 *Cigarette filters*

Due to the described characteristics, thermal resistance and filtering capacity, as well as the relative ease of processing,¹⁹⁰ cellulose acetate also has an application in the production of cigarette filters. In cigarette filters, cellulose acetate is transformed into a fibrous mass by a spinning process (reference). The resulting fibers are then treated with plasticizers and shaped to form a compact, porous cylinder capable of retaining solid particles and certain chemicals present in tobacco smoke. However, the use of cellulose acetate in cigarette filters raises environmental concerns. Although cellulose acetate is of natural origin, as it is derived from cellulose, it undergoes chemical changes that slow its biodegradation, contributing to environmental pollution. The problem of CB accumulation in different environments is mainly due to the slow rate of decomposition because of the high degree of substitution of acetate (~ 2.45), which increases its filtering efficiency but makes it almost inaccessible to microbial decomposition.¹⁹¹ Cigarette butts dispersed in the environment release not only microplastics, but also harmful chemicals derived from tobacco combustion, representing a source of soil and water contamination. A single cigarette butt can contaminate over 1000 Liters of water, posing a significant threat to the quality of urban water sources, including supply reservoirs. Cigarette butts also severely threaten the safety of biological organisms living in these ecosystems, constituting a toxic hazard for a wide range of animals such as snails, crustaceans, insects, and plants. Furthermore, the chemicals present in cigarette butts can interfere with the behaviour of larger birds and fish.¹⁹² CBs can release approximately 7000 chemicals, including over 40 carcinogenic and mutagenic compounds.¹⁹³ Specifically, pollutants released by cigarette butts includes:

- **Heavy metals:** the heavy metals present in cigarette filters originate from the products used in tobacco cultivation and cigarette manufacturing.¹⁹⁴ Among

the metals identified in the filters are lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), iron (Fe), copper (Cu), and tin (Sn). When CBs come into contact with water, metals such as Al, Cd, Pb, and Zn can leach out, affecting both freshwater and marine environments. Factors like the pH of the water, chemical composition, and the contact time between CBs and water influence the type and concentration of heavy metals released.¹⁹⁴ For instance, lower pH levels in leachates from smoked filters promote greater heavy metal solubility. Investigations into the levels of heavy metals in cigarette butts (CBs) in marine and terrestrial environments, such as those conducted in the Persian Gulf, have revealed high concentrations of metals like Cd and Pb.¹⁹⁵

- **Polycyclic aromatic hydrocarbons (PAHs):** Polycyclic aromatic hydrocarbons are produced by the incomplete combustion of organic compounds, including tobacco. They are of environmental concern due to their carcinogenic, mutagenic, and toxic properties, as well as their persistence.¹⁹⁶ The Environmental Protection Agency (EPA) has identified 16 priority PAHs, including naphthalene, anthracene, phenanthrene, and benzo(a)pyrene. CBs, tobacco, and cigarette smoke contain significant levels of PAHs. PAH levels in CBs vary based on environmental conditions. For instance, freshly smoked CBs contain more naphthalene (23.4%) than CBs collected near rivers (4.3%), as lighter PAHs like naphthalene leach into water faster.¹⁹⁷ Heavier PAHs, such as benzo(a)pyrene, persist longer in CBs due to their low volatility and water solubility. Leaching experiments show that PAHs with higher solubility, such as naphthalene and anthracene, are released into water more quickly, whereas heavier PAHs require prolonged contact (21 days) to leach significantly.¹⁹⁷ CBs exposed to various types of water release PAHs into aquatic environments, posing toxicity risks to organisms. Studies highlight the need for further investigation into PAH release under realistic environmental conditions to assess risks to aquatic ecosystems.

- **Nicotine:** Nicotine, an alkaloid found in tobacco, comprises 0.6–3% of its content.¹⁹⁸ Nicotine has a water octanol partition contribution (Kow) of 1.17,¹⁹⁹

indicating high hydrophilicity. Due to its hydrophilicity, nicotine is rapidly released from cigarette butts (CBs) into water. For example, Roder Green et al.²⁰⁰ reported that 7.1 ± 0.07 mg/g nicotine was released from CBs within 1440 minutes, with 50% of the total released in just 27.2 minutes. The amount of nicotine leached into water varies depending on the cigarette's nicotine content, the composition of CBs, and experimental conditions.

The leaching rate is also influenced by CB composition. Dobaradaran et al.²⁰¹ (2024) showed nicotine release levels ranging from 0.17–17.34 mg/g depending on whether ash, aged CBs, or freshly smoked CBs were tested. Long-term estimates suggest 380–7065 tons of nicotine could enter aquatic ecosystems annually from discarded CBs.

- **Aromatic amines and BTEX** (benzene, toluene, ethylbenzene, and xylene) compounds: Carcinogenic aromatic amines are produced during the smoking process, with CBs containing significantly higher levels compared to unsmoked cigarettes. Dobaradaran et al. reported that freshly smoked CBs contain 3.43 $\mu\text{g/g}$ of aromatic amines, 12.2 times higher than unsmoked cigarettes, and 1.62 times higher than aged CBs. This indicates the potential for aromatic amines to leach from CBs into the environment over time. Key aromatic amines identified include aniline (ANL), toluidines, and aminobiphenyls. Among these, ANL had the highest leaching rate into both distilled and river water during contact times ranging from 15 minutes to 30 days.

BTEX compounds (benzene, toluene, ethylbenzene, xylene), highly volatile toxic pollutants, also leach from CBs into water. Dobaradaran et al.²⁰² found that toluene exhibited the highest leachate rate, followed by p-xylene, ethylbenzene, and benzene. BTEX release depends on the time between smoking and water exposure. CBs added to water immediately after smoking released measurable amounts of BTEX, but leachates were undetectable if CBs were exposed to water after 45 minutes or more. This suggests that immediate contact with water, such as from rain or direct disposal, is necessary for significant BTEX release.

- **Microplastics:** Cellulose acetate cigarette filters are also a significant source of microplastics for the environment. Microplastics, defined as plastic particles smaller than 5 mm, pose a significant threat to the environment and aquatic organisms due to their persistence and ability to adsorb pollutants.²⁰³ They originate from primary sources, such as microbeads in cosmetics, and secondary sources, including the breakdown of larger plastics like cigarette filters.²⁰⁴ Cigarette filters, composed of cellulose acetate, degrade slowly, taking up to 30 years, and are a major source of microplastics in the environment. Filters can release around 100 microfibers per day, contributing an estimated 0.3 million tons of microplastics annually to aquatic systems.²⁰⁵

Cigarette butts (CBs), with 845,000 tons discarded annually, are a significant source of microplastics, especially in aquatic environments where a third of CBs end up.²⁰⁶ Microplastics from CB filters can adsorb toxic pollutants like heavy metals and PAHs, which can transfer through the food chain to aquatic organisms and humans.²⁰⁷ However, the characteristics and abundance of cellulose acetate microfibers from CBs, as well as their removal by treatment processes, remain under-researched. Comprehensive studies are urgently needed to better understand the environmental fate of CB-derived microplastics and their implications for ecosystem and human health.

Other pollutants present in cigarette filters include formaldehyde, carbon monoxide, ammonium, and hydrogen cyanide, which contribute to their toxicological impact on the environment.^{193,208}

4.2.2 Reuse of Cellulose Acetate from Cigarette Filters

The current disposal systems for CBs are landfilling and incineration, which are unsustainable and release hazardous contaminants into the environment.²⁰⁹ However, several research groups are evaluating the possibility of using cigarette butts in various applications, divided into different categories:²¹⁰

1. **Cellulose Nano Crystals (CNCs) from CBs:** The recovered CA can be converted into cellulose nanofibers or nanocrystals (CNCs), useful as components

for paper products and high-efficiency filters. In the work of Ogundare et al.,²¹¹ CNC has been isolated from cellulose obtained from CBs. The isolation of cellulose from CBs follows a four-stage sequential process: ethanolic extraction, bleaching, deacetylation, and acid hydrolysis with sulfuric acid. After the first extraction phase, the cellulose acetate is first converted into cellulose fibers (60%) and then into crystalline nanocellulose (49%). CNC is modified and used to remove diclofenac from water²¹² or as an agent for heavy metal adsorption²¹³ or it could be used in catalysis and in the field of biomaterials.²¹¹

2. **As a cheap source of cellulose:** Teixeira et al.²¹⁴ developed a process for producing cellulose pulp from cigarette butts using an alkaline pulping process. The procedure is divided into four main stages: separating chemicals and tar from the filter, converting cellulose acetate into cellulose with NaOH, removing lignin to free cellulose, and finally, disaggregating the residual paper. Purification occurs through a series of reactions, including acidification, coagulation, and ozonation, leading to the precipitation of impurities.
3. **Sorbent for hydrophobic and oleophilic materials:** Waste CBs have been found to be a useful raw material for making oil-absorbing materials, which can be used as hydrophobic and oleophilic substances.²¹⁵ By modifying the fibers of CBs with SiO₂, methyltrimethoxysilane (MTMS), and octadecyltrichlorosilane (OTS), the fibers become hydrophobic and efficient in absorbing oil from oil-water mixtures. Efficiency has been reported as exceeding 99.77%. Additionally, these materials have proven to be durable under challenging conditions and remain stable even after multiple cycles.
4. **Additives for material production:** Cigarette butts can be used as additives in clay bricks and in the metallurgical sector. Mohajerani et al. mixed CBs in varying percentages (up to 10%) via mechanical mixing. Cigarette butts have proven to be an excellent resource for improving brick durability, as well as optimizing thermal behavior, porosity, dimensional reduction, and strength. Incorporating 1% of CBs can reduce energy consumption by up to eightfold. Another example is the reinforcement of natural rubber.^{216,217} Cellulose acetate

fibers from filters can help improve the mechanical properties of rubber because they remain stable up to 300°C, a suitable temperature for most rubber applications. The authors found that adding 4% by weight of cellulose acetate to the material is optimal for improving rheological and mechanical properties.

5. **Corrosion inhibitor agent:** Zhao et al.²¹⁸ demonstrated that certain chemicals in cigarette butts (CBs), such as nicotine, have antiseptic properties and are effective as corrosion inhibitors; the use of recovered cigarette butts has proven functional as corrosion inhibitors for steel in contact with acidic solutions.
6. **Source of porous carbon:** Activated carbon is a material primarily made of carbon with a porous structure, generally characterized by a high specific surface area, which gives it high adsorption capacity. Consequently, the industrial production of activated carbon is used for various applications such as capturing pollutants in gaseous or aqueous phases, gas separation processes, and more. Cigarette butts (CBs) have been considered an alternative raw material for producing activated carbon,²¹⁹ as they contain a high amount of carbon and cellulose, which provide a porous structure. About 58% of cigarette filters are made of carbon. The production of activated carbon from CBs is achieved by treating them with a KOH solution at a temperature of 900°C. Researchers are interested in using activated carbon (CBs) for hydrogen storage due to its high activation temperature, surface area, and porosity. The hydrothermal carbonization of activated carbon produces hydrochar, which has a high surface area and excellent porosity. Upon activation, hydrochar forms an oxygen-rich porous carbon structure capable of storing hydrogen with a weight capacity of up to 9.4%.²²⁰
7. **Insecticidal agent for mosquito vectors:** An interesting application was proposed by Dieng et al.,²²¹ for producing a biocide. This article verified how cigarette butts can affect *Aedes aegypti*, a vector of dengue (a disease also known as tropical flu, transmitted by the mosquito *Aedes*). Exposure to CBs can influence egg-laying behavior, hatching, and the development of *Aedes albopictus* and *Aedes aegypti*. The use of a 2% CB solution demonstrated re-

duced larval survival. Furthermore, nicotine and its derivatives, the main components of CBs, have proven toxic to mosquitoes and other insects, as well as to chloroquine-resistant malaria parasite *Plasmodium falciparum* and certain microbial pathogens.

8. **Binder in asphalt concrete:** CBs have shown improvements in asphalt concrete characteristics, such as flowability, Marshall stability, air void percentage, resilience modulus, and density, with the use of 10 kg/m³ or 15 kg/m³ of CBs encapsulated in bitumen.²²²
9. **Components for electronic devices and energy storage:** CBs can be integrated into electronic devices for various technological purposes. Ghosh et al.²²³ highlighted how the pyrolysis treatment of CBs produces a material with good conductive properties, applicable in various electronic sectors such as energy storage devices.
10. **Alternative materials for sound absorption:** The porous nature of CBs facilitates sound absorption. Gomez Escobar et al.,²²⁴ demonstrated the high acoustic absorption capacity of this material, suggesting its use as an insulating component competitive with commercial solutions.
11. **Agent for Water treatment:** Abu-Danso et al.²¹² studied the use of nanocellulose fibers obtained from CBs to remove pharmaceutical contaminants (such as diclofenac) from water, demonstrating the versatility of recycled CA as a material for water treatment.
12. **Fabrication of aerogels:** CA aerogels derived from cigarette butts were fabricated using an economical freeze-drying method with polyvinyl alcohol (PVA) as a crosslinker. The CA aerogels produced by Chau et al.²²⁵ showed extremely low density (between 0.003 kg/m³ and 0.5 kg/m³), high porosity (80–99.8%), a large specific surface area (100–1600 m²/g), and low thermal conductivity (0.034–0.039 W/(mK)). For comparison, fiberglass has a thermal conductivity between 0.031 and 0.040 W/(mK), and it should be noted that many common materials used for thermal insulation are primarily produced from non-renewable resources and therefore have an environmental impact.

- 13. Synthesis of top value chemicals:** Losito et al.²²⁶ demonstrated that four types of urban waste—cigarette butts, sanitary pant diapers, newspapers, and soybean peels—can be used as cellulose sources for the production of high-value industrial chemicals such as levulinic acid (LA), 5-acetoxymethyl-2-furaldehyde (AMF), 5-(hydroxymethyl)furfural (HMF), and furfural.

5.2.3 Use of Cellulose Acetate as a Support in Catalyst Production

Among its various applications, cellulose acetate (CA) has also been employed in the synthesis of new heterogeneous catalysts as a support material for metal particles. Based on findings from the literature, CA proves to be a versatile and sustainable support material, particularly for removing toxic compounds and degrading organic pollutants, such as dyes, which contribute to water pollution. Some studies utilize cellulose acetate derived from waste, such as cigarette filters, offering an approach to support the circular economy and resource management.

In the study by Teixeira et al.,²²⁷ cigarette filters were used as a carbon source to produce solid carbon acid catalysts intended for esterification reactions. The synthesis involved carbonization and sulfonation of the filters through hydrothermal treatment with sulfuric acid at varying temperatures and durations. The filters were initially washed with water and dried in an oven at 80°C, then treated in an autoclave with sulfuric acid at temperatures ranging from 100°C to 190°C for periods between 2 and 8 hours. The sample exhibiting the best catalytic performance was synthesized at 190°C for 4 hours, achieving a 94% conversion of oleic acid into methyl oleate. Furthermore, this sample was reusable for up to four reaction cycles without a significant loss in efficiency.

Mousa et al.²²⁸ developed an efficient catalyst for the reduction of organic dyes (Rhodamine B, Rhodamine 6G, Methylene Blue, and Sunset Yellow) using sodium borohydride (NaBH₄) and for antibacterial applications (against *Staphylococcus aureus* and *Escherichia coli*). They synthesized an eco-sustainable nanocomposite (Ag-ZnO@CA) from cellulose acetate derived from cigarette filters combined with zinc and silver nanoparticles. After cleaning the filters with water and ethanol, the CA

fiber was dissolved in a mixture of acetone and water (43:7). ZnO nanoparticles were added, and the material was dried to form a film that served as a support for Ag nanoparticles.

In another study by Homdi et al.,²²⁹ cellulose acetate derived from cigarette filters was used as a sustainable material for developing catalysts aimed at removing dye pollutants from water. Powdered mint leaves were mixed with cellulose acetate dissolved in acetone. After washing with distilled water, a porous film was obtained and then impregnated in a 0.05 M solution of CuSO_4 and AgNO_3 . The mint-CA films were then dipped into a freshly prepared 0.1 M NaBH_4 solution to reduce Cu^{2+} and Ag^+ ions into Cu^0 and Ag^0 nanoparticles. The AgNPs@mint-CA demonstrated high catalytic performance.

Cellulose acetate has also been utilized to create stable films²³⁰ by adding cerium/zirconium to a CA dispersion. The resulting film was treated with a CuSO_4 solution, followed by the reduction of Cu^{2+} ions to Cu^0 using NaBH_4 as a reducing agent. These synthesized catalysts were applied in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and the degradation of cationic dyes such as Methylene Blue (MB) and Rhodamine B (RB), proving effective for the simultaneous removal of multiple pollutants.

In the work by Bakhsh et al.,²³¹ the catalyst synthesis began by dissolving cellulose acetate in acetone and incorporating Fe_2O_3 nanoparticles, forming a $\text{CA/Fe}_2\text{O}_3$ thin film through drying. The film was impregnated with solutions of Ag (I), Cu (II), and Ni (II), which were subsequently reduced with NaBH_4 to obtain the final catalysts. These were used for the catalytic reduction of Methyl Orange (MO) and p-nitrophenol (PNP), demonstrating high efficiency in pollutant degradation.

In the study by Kamal et al.,²³² cellulose acetate fibers and sheets were prepared using wet-spinning and doctor blade methods, respectively. These CA materials were immersed in a 0.1 M aqueous AgNO_3 solution, followed by treatment with a 0.1 M NaBH_4 solution to synthesize Ag nanoparticles on the substrates. These materials were tested as catalysts in the hydrogenation of 2,6-dinitrophenol (2,6-DNP) using NaBH_4 .

This extensive range of applications highlights cellulose acetate's versatility and sustainability as a support material in catalytic processes, offering innovative solutions for environmental remediation and industrial applications.

4.3 Characterization of cigarette filters

In this research, cigarette filters supplied by Philip Morris were utilized. Specifically, TEREA brand filters were smoked using a smoke machine to ensure a homogeneous sample. This approach aimed to standardize the starting material for cleaning experiments with various deep eutectic solvents, thereby minimizing error and data variability. The use of filters from different brands, aged under varying environmental conditions and durations, would result in fluctuating levels of pollutants.²³³ Furthermore, the type of smoking, influenced by the individual behavior of smokers, can significantly alter the amount of pollutants retained in the filter. Such variability could obscure whether the cleaning efficiency was due to the DES itself or to differences in the initial conditions of the filters. Ensuring sample uniformity thus enabled a more reliable assessment of DES performance.

TEREA cigarettes are specifically designed for use with the IQOS (I Quit Ordinary Smoking) ILUMA system, an advanced technology for heating tobacco without combustion. Heated tobacco products (HTPs) were first introduced to the market in the 1980s.²³⁴ These devices heat the tobacco from within using a metal foil located at the center of the stick and in direct contact with the tobacco. This innovative approach ensures uniform heating of the tobacco without burning it, thereby eliminating combustion and, consequently, the production of smoke, ash, and many toxic substances typically associated with traditional combustion.

Each TEREA stick is composed of a finely processed tobacco blend, encased in a specially designed wrapper that prevents residue leakage during use. The tobacco is situated between a front seal and a cellulose acetate ventilation chamber, which allows the passage of the optimal amount of vapor. At the same time, the final filter cools the temperature of the tobacco aerosol to a suitable level and retains pollutants present in the vapor. The entire assembly is encased in a protective paper wrapper.

Within the tobacco blend is a metal foil coated with stainless steel, which enables the tobacco to reach the ideal temperature to release a nicotine-rich aerosol. (Figure 46)



Fig. 46²³⁵ - Schematic representation of a TEREА® heated tobacco stick for IQOS ILUMA® induction system.

Unlike traditional cigarettes, which burn tobacco and paper to produce smoke along with a wide range of toxic chemical compounds, the IQOS system with TEREА sticks generates an aerosol containing nicotine and flavors derived from tobacco, without the byproducts of combustion. Various additives are used during the curing processes of tobacco. These additives include humectants such as vegetable glycerine (VG) and propylene glycol (PG), which help deliver nicotine in the aerosols produced by HTPs. However, when heated, these humectants can pose potential risks to users due to the formation of carbonyl compounds (e.g., formaldehyde, acetaldehyde, and acrolein),²³⁶ a class of substances that may be cytotoxic, mutagenic, and carcinogenic.²³⁷

To evaluate the performance of various DES in the filter cleaning procedure, only the final section of the TEREА stick, the cigarette filter tip, was selected for analysis.

The filters were characterized using a combination of different analytical techniques, providing a comprehensive understanding of structural, morphological, thermal, and chemical properties. These techniques were: ATR-FT-IR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric Analysis), SEM (Scanning Electron Microscopy), ¹H NMR Spectroscopy (Proton Nuclear Magnetic Resonance Spectroscopy).

4.3.1 ATR-FTIR analysis

The filter of an unused and used TERE stick were analyzed by ATR-FTIR analysis (Figure 47).

FTIR Spectrophotometry was used to analyze functional groups contained in CA present in unused filters and CB, listed in Tabel 22. The analysis employs wavelengths in the range of $500\text{-}4000\text{ cm}^{-1}$. There is no significant difference between the two spectra in unused filters and CB. It is observed that the two spectra exhibit the same bands, but with intensity changes.

The bands around 3400 cm^{-1} in cellulose acetate are attributed to O-H stretching vibrations, which indicate the presence of water and also the presence of non-acetylated OH groups in the polymer. The peak around 2920 cm^{-1} is attributed to the C-H stretching. The sharp peaks at 1030 cm^{-1} and 1215 cm^{-1} are related to C-O stretching vibrations and C-O-C stretching vibrations in the anhydroglucose ring units. Furthermore, C-O stretching vibrations are also attributed to the acetyl group, accompanied by the C-H bending signal in CH_3 at 1370 cm^{-1} . The band at 1740 cm^{-1} in cellulose acetate, attributed to C=O stretching vibrations in aliphatic esters, confirms the presence of the acetyl group.

A peak at 900 cm^{-1} is noted, corresponding to the deformation vibrations of bonds in COC, CCO, and CCH groups,²³⁸ which is attributed to the amorphous region in cellulose acetate.²³⁹ The peak at 600 cm^{-1} demonstrates the presence of C-H out-of-plane bending vibrations.

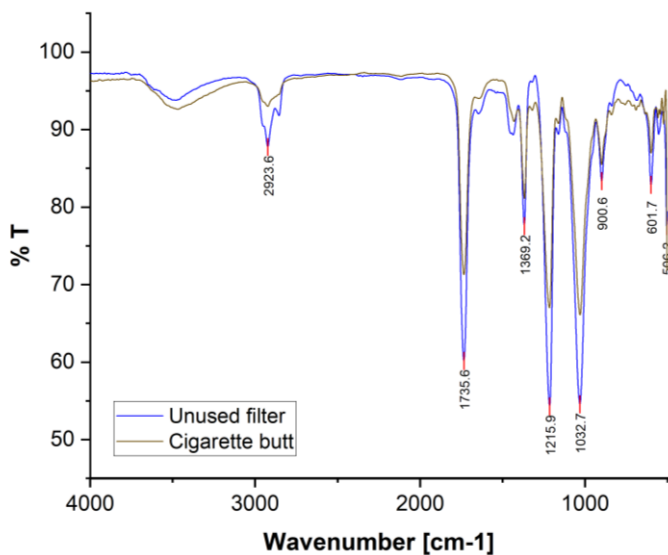


Fig. 47 - ATR-FT spectra comparison of the filter of an unused (blue curve) and used (brown curve) TEREA stick.

Table 22. Characteristic peak assignment of cellulose acetate.

Functional Group Assignments	Wavenumber, cm^{-1}
νOH (covalent bond, hydrogen bonding)	3400 cm^{-1}
νCH	2924 cm^{-1}
$\text{C}=\text{O}$ stretching of the acetyl group	1736 cm^{-1}
δCH_2 ((symmetric); crystalline region)	1430 cm^{-1}
$\text{C}-\text{H}$ bending vibration of CH_3 in the acetyl group)	1369 cm^{-1}
δCH_2 (wagging at C-6) or δCOH in a plane at C-2 and C-3	1320 cm^{-1}
$\text{C}-\text{O}$ stretching of the acetyl group	1216 cm^{-1}
νCO , δOH (γCOC at β -glycosidic linkage)	1160 cm^{-1}
γ -ring in plane	1120 cm^{-1}
$\nu\text{C}-\text{O}$ ($\text{C}-\text{O}-\text{C}$ of the cellulose backbone)	1033 cm^{-1}
δCH_2 (γCOC at β -glycosidic linkage; amorphous region)	901 cm^{-1}

4.3.2 *Thermogravimetric analysis*

Thermogravimetric analyses (TGA) were performed under nitrogen flow (40 mL min⁻¹) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 700 °C with a heating rate of 10 °C min⁻¹.

The TGA of cigarette filters (Figure 48a) reveals multiple phases of mass loss, each associated with the decomposition of specific components within the filter. The thermogravimetric curves exhibit three different temperature ranges, each correlated with specific thermal events, the first from 30 to 250 °C, the second from 250 to 500 °C, and the third beyond 500 °C. During the first range, a minor weight loss (3–5%) was observed up to 100 °C, attributed to the evaporation of residual moisture.²⁴⁰ It was further noted that within this range (above 100 °C), while the weight of the reference cellulose acetate (CA) powder remained nearly constant until decomposition initiated at 270 °C, the CA fibers from the cigarette filters, both unused and used, exhibited progressive pyrolysis up to this temperature. This behavior was due to the degradation of light volatiles and plasticizers²¹⁰ such as glycerol, whose presence was confirmed by ¹H NMR spectra (Figure 53). The weight loss in this stage was 13% and 17% for the unused and used cigarette filters, respectively. Thus, as expected, we observe that the greatest mass loss in this temperature range is attributable to the used filter, due to the presence of contaminants deposited during the cigarette smoke filtering process that begin to evaporate or decompose at low temperatures. The greater slope of the cigarette butt TGA curve thus reflects the volatilization and degradation of these additional substances, which are not present in the unused filter, confirming the influence of smoke residue on thermal behavior in this temperature range.

The derivative thermogravimetric (DTG, figure 48b) curves further illustrate this difference, in the same temperature range, showing a peak at 190 °C for the used filter and two distinct peaks at 156 °C and 210 °C for the unused filter.

In the second temperature range (250–450 °C), a significant weight loss was observed in the active pyrolytic zone, where the maximum weight reduction (88%) occurred. This stage was primarily attributed thermal degradation of cellulose acetate and other organic substances such as tar and nicotine (350–450 °C).^{241, 242} in the

case of cigarette butt. The DTG analysis (Figure 48b) revealed that the most rapid and significant mass loss occurred at approximately 373 °C for cellulose acetate powder and for unused filter, while the temperature, in the case of cigarette butt is slightly lower (371°C)

Beyond 500 °C, the weight loss slowed considerably, indicating the onset of carbonization and the formation of a more stable char structure. In this stage, cellulose acetate fibers decomposed further.²⁴³

Finally, non-decomposed elements remained as a fraction of solid residue in the form of carbon black particles and/or ash content.

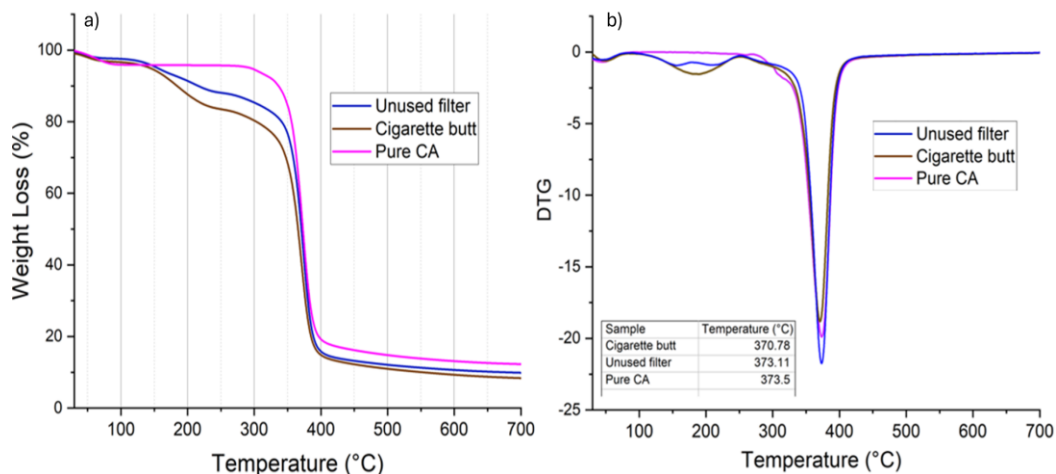


Fig. 48 - (a) Thermogravimetric analysis (TGA) and (b) Derivative thermogravimetric (DTG) curves of cigarette filters (unused and used) and pure cellulose acetate

4.4 Cigarette butts cleaning procedure

The process of recovering cellulose acetate from used cigarette filters includes a washing phase to remove impurities and harmful substances. During this phase, the filters are immersed in acidic H_2SO_4 solutions to remove metals, followed by treatment with specific solvents aimed at eliminating organic impurities such as absolute

ethanol,²¹⁰ diethyl ether, and hexane.²⁴⁴ Generally, the cleaned filters are dissolved in acetone, and distilled water is added until a white precipitate of cellulose acetate is formed.

In this work, Deep Eutectic Solvents (DES) were employed as innovative solvents for cleaning cigarette filters. DESs represent a sustainable and efficient alternative to traditional solvents due to their low toxicity, biodegradability, and ease of preparation.

4.4.1 *Deep Eutectic Solvents: classification, properties and applications*

Deep eutectic solvents are an emerging category of solvent that have attracted the attention of the scientific community due to their environmentally friendly properties and their versatility in many applications. These solvents are a mixture of two or more compounds that are generally solid at room temperature but, when they are combined in a specific molar ratio, form a liquid solution, i.e., a decrease in the melting point is observed for these mixtures because of the interaction between the molecules.²⁴⁵ Over the last two decades, they have drawn significant interest following a study by Abbott et al.,²⁴⁶ which revealed an unusual depression of the melting point at the eutectic composition of certain hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). This distinctive behavior was initially observed in a 1:2 molar ratio mixture of choline chloride in powdered form ((2-hydroxyethyl)-trimethylammonium chloride) [melting point, $T_m \approx 302\text{ }^{\circ}\text{C}$] and solid urea [$T_m \approx 133\text{ }^{\circ}\text{C}$], known as "reline". The resulting combination remain liquid at ambient temperature [eutectic mixture melting point, $T_{\text{eutectic}} = 12\text{ }^{\circ}\text{C}$]. Abbott *et al.* called the liquid a "deep" eutectic mixture (DEM) to describe the phenomenon. Since the properties of these liquids are their main point of interest, common terminology has adopted the term "deep eutectic solvent" as a general label for this distinct class of materials.²⁴⁷

DES are closely associated with ionic liquids (ILs),²⁴⁸ and have sometimes been confused with them.²⁴⁹ Certainly, DESs are natural competitors of ILs, since they exhibit several shared properties. However, these two solvent types differ significantly for two main reasons. Firstly, their constituent materials are fundamentally distinct:

ILs are composed of organic cations paired with organic or inorganic anions and are primarily governed by ionic interactions while DESs arise from the combination of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) and are characterized by strong hydrogen-bonding interactions.

Secondly, their preparation methods differ notably: DESs are typically obtained by simple heating processes of their components, whereas ILs generally require more complex synthetic procedures involving multiple reagents and solvents, usually consisting of two main steps—cation formation followed by anion exchange.²⁵⁰

Given that the presence of a eutectic point or hydrogen bonding between components is not sufficient conditions to define a “deep eutectic solvent” and in order to clarify what a deep eutectic solvent is and what makes it special compared to other mixtures, Martins et al.²⁵¹ recently defined deep eutectic solvent as “a mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from ideality”, (Figure 49) In this case $\Delta T_2 > 0$, where ΔT_2 stands for the temperature depression which is the difference between the ideal (red curve Figure 49) and the real (green curve, Figure 49) eutectic point. The eutectic point represents the composition and the minimum melting temperature at which the melting curves of both compounds meet

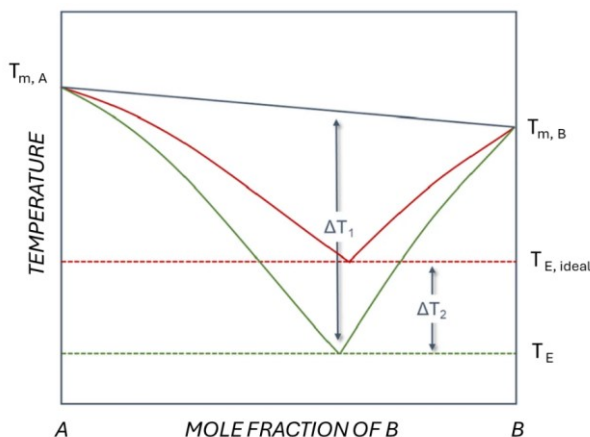


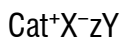
Fig. 49 - Solid-liquid phase diagram of a binary mixture illustrating the difference between an ideal and a real deep eutectic solvent system. $T_m(A)$ and $T_m(B)$ represent the melting temperatures of compounds A and B, respectively. The eutectic point marks the composition and temperature at which both compounds melt simultaneously. The red curve represents the ideal eutectic behavior, while the green curve shows the real behavior of a DES system, highlighting a significant temperature depression ($\Delta T_2 > 0$) compared to the ideal mixture.

Hydrogen bonds are considered one of the main intermolecular forces responsible for the melting point depression observed in DESs, alongside steric effects and ionic interactions between anions and cations. According to an IUPAC study,²⁵² a hydrogen bond is inherently electrostatic in nature, involving a charge transfer between the HBD and the HBA. This transfer can generate a "partially covalent" bond, which can be detected through techniques such as FTIR spectroscopy.²⁵³ However, the network of these bonds varies significantly depending on the components used in the DES, greatly influencing their macroscopic properties. In particular, in the most studied systems, such as ChCl:Ethylen Glycol, ChCl:Glycerol, and ChCl:Urea, distinct behaviors emerge.²⁵⁴ In the case of ChCl:Ethylen Glycol, the addition of choline chloride tends to strengthen the pre-existing hydrogen bonds in the ethylene glycol structure. This system achieves its maximum density at the eutectic ratio of 1:2, suggesting a stable and well-organized network of intermolecular interactions. Conversely, in the ChCl:Glycerol system, the addition of choline chloride tends to disrupt the naturally occurring hydrogen bonds in glycerol. As a result, the maximum density is not observed at the eutectic ratio (1:2) but rather at a 1:4 ratio, suggesting that the addition-

al -OH groups in glycerol create a more complex and vulnerable network prone to disruption by choline chloride. The ChCl:Urea system, on the other hand, behaves in an even more peculiar manner. In this case, the dominant interactions occur between urea molecules themselves (HBD-HBD) rather than between urea and choline chloride. This phenomenon leads to a hydrogen bond network entirely different from the previous systems, with unique characteristics that cannot be easily generalized.

These differences highlight a crucial point: there is no universal model to explain hydrogen bond formation in DESs. Each combination of HBA and HBD creates a distinct and specific hydrogen bond network, with unique dynamics and macroscopic properties.

DES can be generally described by the formula:



where Cat^+ represents, any ammonium, phosphonium, or sulfonium cation, while X^- is a Lewis base, typically a halide anion. Complex anionic species are formed between X^- and a Lewis or Brønsted acid Y, where z indicates the number of Y molecules interacting with the anion.²⁵⁵

The majority of DESs prepared and studied so far are traditionally classified into four main types (Figure 50):

- Type I: A combination of a quaternary ammonium salt and a metal chloride (MCl_x).
- Type II: Composed of a quaternary ammonium salt and a metal chloride hydrate. The relatively low cost of many hydrated metal salts, along with their stability against air and moisture, makes them suitable for large-scale industrial processes.²⁵⁶
- Type III: Formed by a quaternary ammonium salt and a HBD, typically an organic molecular component such as an amide, carboxylic acid, or polyol.
- Type IV: A mixture of a metal chloride hydrate and an HBD.

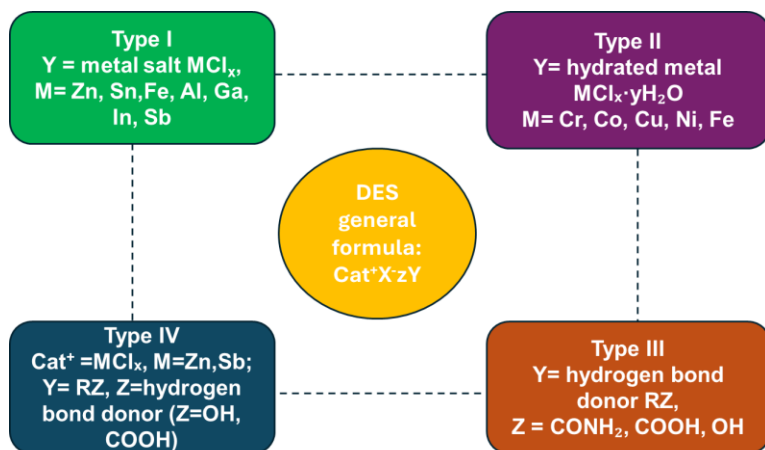


Fig. 50 - Classification of Deep Eutectic Solvents (DESs) into four main types.

The preparation of deep eutectic solvents (DES) can involve different methodologies, including heating²⁵⁷ and grinding.²⁵⁸ In the heating method, the components are mixed and heated under stirring until a homogeneous liquid is obtained.²⁵⁷ Typically, the temperature is maintained between 50 and 100 °C. However, elevated temperatures may cause degradation of the solvent, often through esterification reactions, particularly in systems involving choline chloride and carboxylic acids.²⁵⁹

On the other hand, the grinding method involves combining the components at ambient temperature and manually crushing them using a mortar and pestle until a transparent liquid is formed. This approach avoids potential thermal degradation associated with higher temperatures.²⁶⁰

The physicochemical properties of deep eutectic solvents represent the main reasons for the growing interest of the scientific community in these materials. In addition to exhibiting low volatility, non-flammability, low vapor pressure, and remarkable chemical and thermal stability, deep eutectic solvents offer significant chemical flexibility, allowing them to be tailored for specific applications thanks to the wide range of compounds that can be used in their formulation.²⁶¹

One of the most significant properties is their viscosity, which is generally high at room temperature due to the dense network of hydrogen bonds between the components. However, this property can vary considerably: some DES, such as cho-

line chloride:ethylene glycol (1:2), exhibit very low viscosities, while others, like mixtures based on metal salts, can reach extremely high values.²⁶² Viscosity is influenced by the nature of the components,²⁶³ the molar ratio,²⁶⁴ temperature,²⁵⁷ and water content.²⁶⁵

Density, a fundamental property of liquids, varies widely among DESs. Most DES exhibit densities higher than water, typically ranging from 1.0 to 1.3 g/cm³ at 25 °C, with metal salt-based DES reaching up to 1.6 g/cm³.²⁶⁶ In contrast, hydrophobic DES often have densities below that of water.²⁶⁰ The density of DES decreases linearly with temperature²⁶⁷ and is influenced by the choice of hydrogen bond donor and molar ratio,²⁶⁸ highlighting their nature for specific applications.

Ionic conductivity is closely related to viscosity: as the temperature increases, viscosity decreases, and conductivity rises.²⁶⁹ However, DES generally tend to have low ionic conductivity. Factors such as the hydrogen bond acceptor-to-donor ratio,²⁵⁷ the nature of the components,²⁷⁰ and water content play a crucial role.²⁶⁵

Surface tension is an additional property of DES. Deep eutectic solvents with high viscosity often exhibit high surface tension values, which decrease linearly with increasing temperature. The type of cation and the molar fraction of the salt also influence this property.²⁷⁰

Another important factor influencing the behavior of DES is water content, which, due to the hygroscopic nature of some DES components, is often unavoidable and plays a crucial role in their physical properties.²⁷¹ Even small amounts of water can drastically reduce viscosity, increase conductivity, and affect polarity. At low water content, water acts as an additional hydrogen bond donor, strengthening the DES network. However, at higher levels, it can interfere with interactions between components, altering the supramolecular structure of the system.²⁷²

In summary, the properties of DES are highly tunable and strongly depend on their chemical composition, the molar ratio of the components, temperature, and water content. This gives DES immense application potential but requires further studies to optimize their use in specific contexts.

DES have applications in numerous fields due to their versatility, low cost, environmental sustainability, and chemical and physical properties.

DES are used for metallurgic applications, in the extraction, recovery and refining of metals.²⁷³ Due to the high solubility of metal salts and their electrical conductivity, DES are suitable for electrodeposition of metals and alloys such as zinc, nickel and cobalt.²⁷⁴ In addition, they are used to dissolve and recover precious metals such as gold and tellurium.²⁷⁵

DES are used in the separation of azeotropic mixtures and in the extraction of volatile fatty acids from aqueous solutions.²⁷⁶ For example, DES based on glycerol and ethylene glycol have shown high selectivity in extraction processes.²⁷⁷ Deep eutectic solvents (DES) have shown promising properties to address some challenges of CO₂ capture. Some DES have shown promise due to their high CO₂ solubility, low vapor pressure and high thermal stability compared to conventional aqueous amines.²⁷⁸ DESs are used as synthesis media for metal nanoparticles and nanostructured materials. They can facilitate the formation of nanomaterials with specific properties for advanced applications in catalysis, medicine and energy.²⁷⁹ They are also applied in the treatment of lignocellulosic biomass to improve the efficiency of material breakdown and extraction of bioactive compounds.^{280, 281} In pharmaceuticals, DESs are studied as solvents for the synthesis of active ingredients and to improve the bioavailability of poorly soluble drugs.²⁸² DES are also applied to extract and recycle valuable components from industrial waste, for instance food industry,²⁸³ thus contributing to a circular economy and waste reduction.

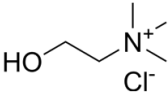
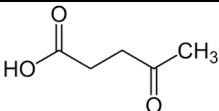
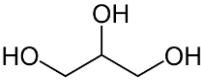
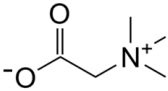
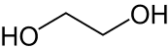
For all these reasons, DES are confirmed as extremely versatile tools in extraction and separation processes, being effective in replacing traditional solvents. The possibility of recycling and low environmental impact makes them key in the development of sustainable and environmentally friendly industrial processes.

4.4.2 DES as Innovative solvents for Cleaning Cigarette Filters

In this study, four distinct DES mixtures were investigated, as detailed in Table 23 DES were synthesized by combining hydrogen bond donors (HBD) (levulinic acid,

glycerol and ethylen glycol) with a quaternary ammonium salt as the hydrogen bond acceptors (HBA) (choline chloride and betaine).

Table 23. Composition of four distinct DESs using hydrogen bond donors (HBD), including levulinic acid, glycerol, and ethylene glycol, combined with hydrogen bond acceptors (HBA) such as choline chloride and betaine.

HBA	HBD	DES abbreviation and HBA:HBD molar ratio
 Choline Chloride (ChCl)	 Levulinic Acid (LevAc)	ChCl:LevAc (1:3)
		ChCl:Gly (1:3)
	 Glycerol (Gly)	Bet:Gly(1:3)
 Betaine (Bet)	 Ethylen Glycol (EtGly)	ChCl:EtGly (1:2)

The DES composed of choline chloride and levulinic acid (ChCl:LevAc) in a 1:3 molar ratio was selected as a potentially useful material for innovative applications, such as the cleaning of cigarette butts, because this DES has demonstrated high efficacy in previous studies for the dearomatization process of gasoline. In fact, in a study conducted by Larriba et al.,²⁸⁴ the ability of such DES to extract aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes, from gasoline mixtures was evaluated. The results highlighted that the 1:3 molar ratio between ChCl and LevAc was the most effective in enhancing the extraction capacity of aromatic compounds, making this DES particularly promising for similar applications.

DESs containing glycerol were selected due to their relevance to circular economy principles. Glycerol is a byproduct generated in large quantities during the transesterification process for biodiesel production. Its integration into DESs not only utilizes a waste material but also contributes to more sustainable resource manage-

ment, reducing environmental impact and promoting the reuse of waste in new production cycles. The use of glycerol as a component of DESs for cigarette filter cleaning, therefore, transforms an industrial byproduct into a valuable resource for advanced chemical applications.

In particular, the DES ChCl:Gly has also been used in desulfurization, denitrification, and dearomatization processes of liquid fuels, demonstrating a greater affinity for pyridine compared to thiophene and toluene, making it particularly useful for the removal of nitrogen-containing compounds.²⁸⁵

The DES Bet:Gly has been utilized for the separation of phenolic compounds from coal tar,²⁸⁶ demonstrating an extraction efficiency of 94.6%.

The DES ChCl:EtGly has been used as lixiviants for cobalt recovery from lithium-ion battery cathode materials²⁸⁷ and it could be useful in removing metals from cigarette filter.

In the present work, the DESs were prepared using the heating method, which involves mixing the components under constant stirring and heating them until a homogeneous and clear liquid is obtained. The preparation was carried out at a temperature of 50 °C, maintained for the time necessary to ensure the formation of a clear and stable mixture. In this case, the choice to maintain the temperature at 50 °C was driven by the need to minimize the risk of component degradation while ensuring the formation of a stable and efficient deep eutectic solvent for the intended application of cigarette butt fiber purification.

4.5 Filter cleaning procedure

The filter cleaning procedure was started with a preliminary preparation step to isolate the cellulose acetate filter to allow subsequent chemical treatment. At this initial stage, the paper lining the TEREA sticks was manually removed, allowing the filter to be recovered. Each filter was then placed whole inside a vial and immersed in selected DES at a filter:DES weight ratio of 1:50. The vials were kept under constant agitation for 2 hours to promote filter cleaning and the system was maintained at a controlled temperature of 50°C. (Figure 51)



Fig. 51 - Experimental setup: TERE filter immersed in DES inside a vial with a magnetic stir bar

The weight ratio of 1:50 was chosen to ensure adequate immersion of the filter in DES, allowing proper penetration of DES throughout the cellulose acetate matrix and thus effective interaction between the solvent and the contaminating particles, while avoiding excessive consumption of DES.

At the end of the treatment, each filter was removed from the vial and washed five times with distilled water in order to completely remove any residual DES. This procedure was successfully performed for all the DES analyzed, except for the DES $\text{ChCl}:\text{LevAc}$. In this specific case, a different behavior was observed as the filter completely dissolved into the solvent after two hours (Figure 47a). For this reason, to recover the filter and to facilitate the precipitation of cellulose acetate, distilled water was incrementally added to the DES solution. This water addition destroyed the DES-cellulose matrix, leading to the visible precipitation of cellulose acetate from the solvent; indeed, an initially transparent precipitate was observed, which subsequently turned white with the increasing addition of water. The precipitated cellulose acetate was subsequently recovered through centrifugation (Figure 47b). To ensure complete removal of DES residues and enhance the purity of the recovered cellulose acetate; the material underwent five washing cycles with distilled water, heated to 85°C.

The recovered cellulose acetate was dried in an oven overnight at 35°C. The dried CA was then shredded with a mortar to obtain a fine powder. (Figure 47c)

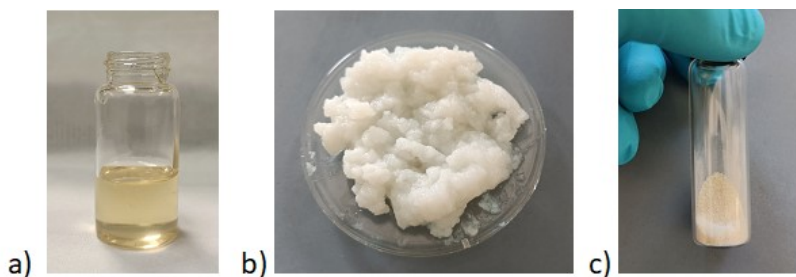


Fig. 52 - (a) Complete dissolution of the cigarette filter in DES ChCl:LevAc after two hours at 50°C. (b) Precipitation of cellulose acetate upon incremental addition of distilled water to the DES solution, followed by recovery through centrifugation. (c) Final cellulose acetate product after drying at 35°C overnight and subsequently mechanical shredding into a fine powder using a mortar.

The dissolution of the cellulose acetate filter in the DES might be linked to the interaction that some DES have with cellulose. It has been demonstrated that Choline Chloride-based Deep Eutectic Solvents can hydrolyse amorphous cellulose, thus promoting its depolymerization.^{280,281} Zhang et al.²⁸⁸ studied four ChCl-based solvents, finding that the order of cellulose dissolution was oxalic acid/ChCl > citric acid/ChCl > urea/ChCl > glycerol/ChCl. Furthermore, it has been observed that ChCl-based solvents with carboxylic acids can dissolve amorphous cellulose.²⁸⁹ In particular, dicarboxylic acids/ChCl DES showed greater efficiency in dissolving and degrading cellulosic fibers compared to monocarboxylic acids/ChCl. A high temperature enhanced cellulose degradation by promoting reducing hydrogen bond rupture between adjacent chains and catalysing ether hydrolysis.

4.6 Characterization of filters after DES treatment

The filters treated with DES were characterized using ATR-FT-IR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric Analysis), SEM (Scanning Electron Microscopy), ¹H NMR Spectroscopy (Proton Nuclear Magnetic Resonance Spectroscopy).

4.6.1 FT-IR analysis

FT-IR analyses were conducted in the wavenumber range of 4000–500 cm^{-1} (Figure 53). The results show that the IR spectra of each filter treated with the different DES analyzed exhibit a similar behavior. No significant differences were observed among the spectra, all of which display the characteristic peaks of cellulose acetate, as reported in Table 21.

This indicates that, after the water washing processes, the DES used to treat the filters are completely removed. Indeed, the spectra show no additional signals that could be attributed to residual DES. These findings confirm the effectiveness of the washing process in fully eliminating any traces of DES while preserving the chemical structure of the base material, cellulose acetate.

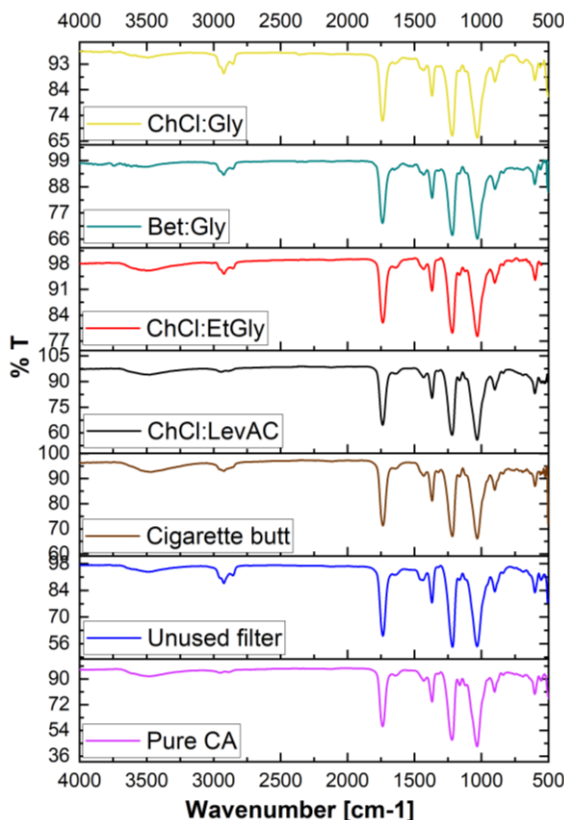


Fig. 53 – ATR-FT spectra of pure cellulose acetate, unused filter, and cigarette butts treated with different DESs.

4.6.2 Thermogravimetric analysis

Thermogravimetric analyses were performed under nitrogen flow (40 mL min^{-1}) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$.

In Figure 54a, the thermogravimetric curves of cigarette filters treated with DES are shown, compared with the curves of unused cigarette filters, cigarette butts, and pure cellulose acetate powder. The thermogravimetric curves, in this case as well, exhibit three distinct temperature ranges: from 30 to 250°C , from 250 to 500°C , and beyond 500°C .

For all analyzed samples, in the first temperature range, up to 100 °C, a slight weight loss (3–5%) is observed, attributed to the evaporation of residual moisture. [Masoudi] Above 100 °C and up to approximately 250 °C, the behavior of the curves for filters cleaned with DES diverges from that of both unused filters and cigarette butts, which show progressive pyrolysis up to this temperature. Conversely, the behavior of the curves for DES-treated filters resembles that of pure cellulose acetate, where the weight remains nearly constant until decomposition begins at around 270 °C. This behavior suggests that DES have been effective in removing light volatiles and plasticizers.²¹⁰

In the second temperature range, the most significant mass loss is observed in all cases, attributed to the thermal degradation of cellulose acetate and the contaminants deposited during the cigarette smoke filtration process, which were not completely removed by the DES. The DTG analysis (Figure 54b) reveals that the most rapid and significant mass loss occurs at approximately 373 °C for all samples.

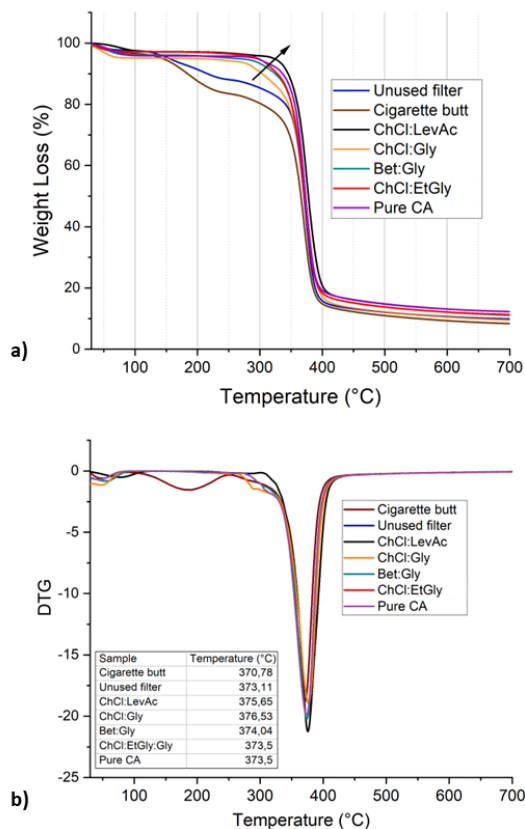


Fig. 54 - (a) Thermogravimetric analysis (TGA) and (b) Derivative thermogravimetric (DTG) curves of pure cellulose acetate, cigarette filters (unused and used) and four cigarette butts treated with different DES

4.6.3 ^1H NMR analysis

^1H NMR spectra were recorded using DMSO- d_6 as the solvent. Analysis by proton nuclear magnetic resonance (NMR) spectroscopy was performed to characterize the chemical content of unused, used, and cleaned cigarette filters (Figure 55).

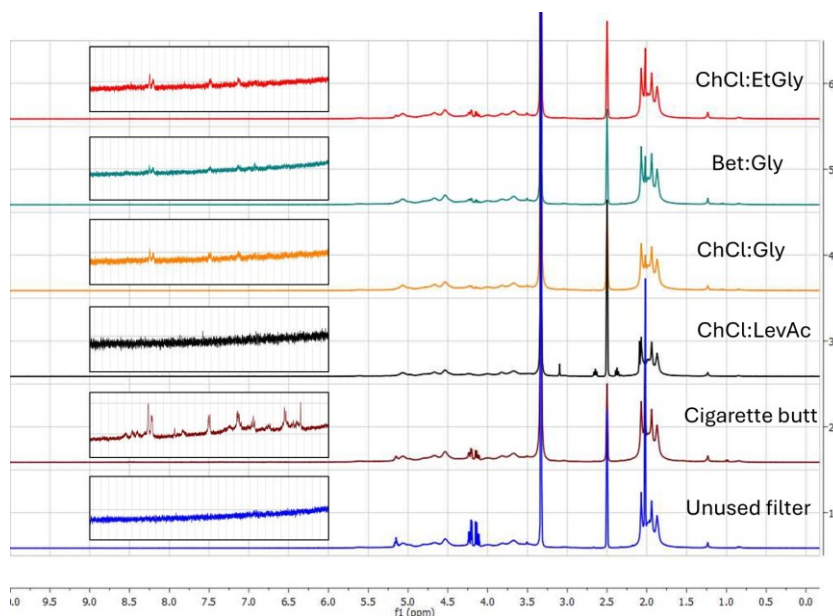


Fig. 55 - ^1H NMR spectra of unused, used, and cleaned cigarette filters recorded in DMSO-d_6 .

The NMR spectrum for unused cigarette filters showed an almost complete absence of signals in the chemical region characteristic of aromatic protons (6.5-8.5 ppm). This observation is consistent with the fact that the unused filters were not exposed to tobacco combustion products, which contain a variety of aromatic compounds.

In contrast, the NMR spectrum of the used filters shows very intense signals in the aromatic region. This result indicates a significant accumulation of aromatic compounds in the filters as a result of their use during smoking. These compounds are mainly derived from tar and other substances in cigarette smoke. NMR spectra obtained from the DES treated filters were analyzed to evaluate the effectiveness of each DES in removing aromatic compounds. The NMR spectrum of the filter cleaned with DES ChCl:LevAc did not show signals in the aromatic region, indicating their effective removal. The same result was not observed for filters cleaned with the other DESs analyzed. This finding suggests that DES ChCl:LevAc was the most efficient in

the cleaning process, demonstrating its effectiveness also in removing glycerol used as a plasticizer.

4.7 Evaluation of filter purity after DES treatment using TGA analysis

Through thermogravimetric analysis (TGA), it was possible to evaluate the purity of cigarette filters treated with DES.²⁹⁰ The widely used mathematical model of Broido²⁹¹ was employed, an analytical method often applied to extract kinetic parameters from TGA curves, such as the reaction order and activation energy, and frequently utilized in the study of TGA behavior of cellulose (add references). This method has demonstrated, through theoretical curves, the utility of this analytical approach in detecting minor experimental deviations caused by small amounts of impurities in the sample or irregularities in the experimental apparatus.

The calculated activation energy provides valuable insights into the purity of the treated cigarette filters. The method is particularly suitable for non-isothermal analyses, where the temperature is a linear function of time, as in this case. By applying this methodology, it will be possible to determine which DES used for filter cleaning was the most effective.

The Broido model uses the following mathematical function to linearize thermogravimetric data and calculate the activation energy (E_a):

$$\ln \left[\ln \left(\frac{1}{y} \right) \right] = - \left(\frac{E_a}{R} \right) \left(\frac{1}{T} + K \right) \quad \text{Equation 5}$$

Where:

- $y = \frac{W_t}{W_{0t}}$: is the normalized weight, calculated as the ratio between the residual mass at a given temperature T (W_t) and the initial sample mass (W_0).
- E_a : is the activation energy, expressed in $\text{kJ K}^{-1} \text{ mol}^{-1}$.
- R : is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).
- T : is the absolute temperature (Kelvin).
- K : is a constant dependent on the pre-exponential factor (A) from the Arrhenius equation.

where T represents the absolute temperature, R is the universal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$) and y the normalized weight (W_t/W_o).

$[\ln(1/y)]$ vs. $1/T$ provides an extremely sensitive method of detecting small deviations in an otherwise simple, unique pyrolysis reaction. Using this equation, thermogravimetric data are transformed into a linear graph, from which the activation energy (E_a) can be calculated using the slope of the resulting linear fit.

The Broido method assumes that the decomposition process follows first-order kinetics. If the graph obtained from the specified equation (Equation 5) is linear, this confirms that the decomposition process can be described as a single first-order reaction, without the interference of overlapping multiple processes. For this reason, it is crucial to select a temperature range that is representative of the decomposition process of interest, avoiding the influence of secondary effects or reaction overlaps.

By analyzing the derivative thermogravimetric (DTG) curves, a temperature range of 360–380 °C was selected, corresponding to the decomposition of the main material. This range was chosen to ensure that the calculated kinetic parameters specifically reflect the targeted decomposition mechanism.

In Figure 56, the linear fits relating to the seven samples considered are shown, confirming the validity of the kinetic model applied to the selected temperature range. The linearity of the plots suggests that the thermal decomposition process follows first-order kinetics, in agreement with the Broido method. A linear fitting of the curves was performed, and the slope of each line was directly correlated with the activation energy (E_a) using the following equation:

$$\text{slope} = -\frac{E_a}{R} \quad \text{Equation 6}$$

The activation energy obtained by the Broido method in Figure 56 using the Arrhenius equation at temperatures ranging from 360 to 380°C are presented in Table 24.

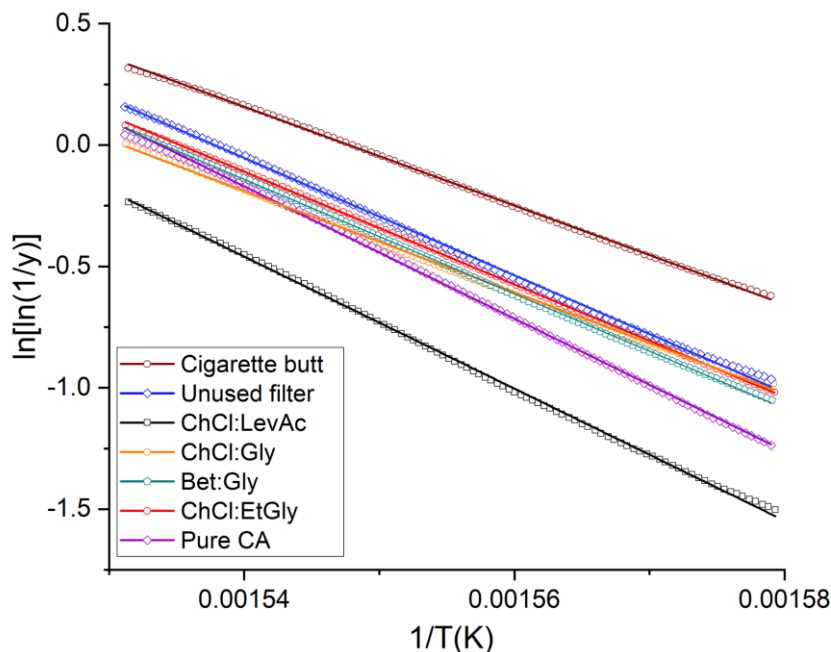


Fig. 56 - Broido diagram of resulting samples

Table 24. Activation energy for filters degradation.

Sample	Linear equation	Ea (kJ K ⁻¹ mol ⁻¹)	R ²
Cigarette butt	Y=-20359,36+31,51	169,2	0.99951
Unused filter	Y=-24173,32+37,17	200,9	0.99907
ChCl:LevAc	Y=-27197,2+41,42	226	0.99942
ChCl:Gly	Y=-20900,92+32	173,7	0.99894
Bet:Gly	Y=-23589,2+36,19	196	0.9998
ChCl:EtGly	Y=-23203,21+35,62	192,8	0.99987
Pure Ca	Y=-27246,23+41,79	226,4	0.99946

From the activation energy (Ea) values listed in the Table 24, it can be observed that the used cigarette filter (cigarette butt) exhibits the lowest Ea (169.2 kJ/mol) among all the analyzed samples. This result is consistent with expectations, as the impurities retained in the filter reduce the stability of the thermal decomposition process. The unused filter shows a significantly higher activation energy (200.9 kJ/mol) compared to the cigarette butt. The highest activation energy is observed for

pure cellulose acetate ($E_a=226.4 \text{ kJ/mol}^{-1} \text{ K}^{-1}$), indicating highly stable thermal decomposition, which is consistent with a pure compound.

Considering the E_a values recorded for the filters after cleaning with different DESs, the highest value, and therefore the purest filter, was obtained after cleaning with the DES composed of Choline Chloride:Levulinic Acid (1:3) ($E_a=226.0 \text{ kJ/mol}^{-1} \text{ K}^{-1}$). In particular, this value is not only the highest among the analyzed DES-treated samples but also exceeds that of the unused filter and is nearly identical to the activation energy of pure cellulose acetate. The two values differ only in the first decimal place. NMR analyses further confirmed the complete absence of aromatic compounds and glycerol in the filter cleaned with this DES.

The other three DES-treated samples show activation energy values between that of the unused filter and the cigarette butt. Specifically, in ascending order, $E_a=173.7 \text{ kJ/mol}^{-1} \text{ K}^{-1}$, for Choline Chloride:Glycerol, $E_a=192.8 \text{ kJ/mol}^{-1} \text{ K}^{-1}$ for Choline Chloride:Ethylene Glycol, and $E_a=196.0 \text{ kJ/mol}^{-1} \text{ K}^{-1}$ for Betaine:Glycerol. Among these, Choline Chloride:Glycerol exhibits the activation energy closest to that of the cigarette butt, indicating that it was the least effective DES in the filter cleaning process. The NMR analyses confirmed the results obtained using the Broido model. Filters cleaned with the DESs ChCl:EtGly Bet:Gly, and ChCl:Gly showed signals in the aromatic region, further corroborating the incomplete removal of impurities in these samples.

4.8 Synthesis of Nickel Catalyst Supported on calcined Cellulose Acetate Ni/calc-CA

Cellulose acetate obtained from cleaning cigarette filters treated with DES ChCl:LevAc, used in a molar ratio of 1:3, was used to prepare the catalyst. This DES proved to be the most effective in removing pollutants. The filter treatment was carried out following the previously described cleaning procedure, which involves dissolving the filter in the DES and subsequently precipitating the cellulose acetate through the gradual addition of distilled water. The recovered material, after multiple washing cy-

cles and thorough drying, appears as a fine and uniform powder, ideal for use as a support for metal particles.

The first step in the catalyst synthesis involved impregnation of the cellulose acetate with a nickel salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) solution. For this purpose, 1 g of cellulose acetate was immersed in 20 mL of a solution prepared by completely dissolving 1 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water. After careful manual stirring to ensure uniform distribution, the mixture was placed in an oven at 85 °C overnight, allowing for complete drying of the impregnated support.

The impregnated material was then calcined for 4 hours at 300 °C in a hydrogen atmosphere, resulting in the formation of a Ni-based black powder, whose organic support was different from the initial cellulose acetate, but still an efficient carbonaceous catalytic matrix, requiring a deeper characterization (Figure 57) This calcination step is crucial for enhancing the adhesion of nickel to the organic support, ensuring the catalyst's stability.

The importance of the calcination step was further highlighted by experimental tests: when the reduction with NaBH_4 was performed without prior calcination, nickel detachment from the cellulose acetate support occurred, leading to the formation of a heterogeneous powder with black and white regions. This confirms that thermal treatment is crucial for ensuring strong adhesion of the nickel particles to the support.



Fig. 57 - Catalyst after the calcination process at 300 °C in a hydrogen atmosphere.

4.9 Catalytic Activity of Ni/calc-CA in the FAMES Upgrading Reaction

Ni/calc-CA and NaBH_4 in appropriate molar ratio were added to a solution of biodiesel (250 mg) in methanol (5.0 mL) in a 25 mL three-necked round flask, equipped with a magnetic stirrer and a gas bubbler. (Figure 58) The whole mixture was left under stirring at room temperature for the appropriate amount of time. The progress of the reaction was monitored by GLC and GC-MS analyses. At the end of the reaction, the catalyst was removed of the liquid phase and washed with methanol (3 x 5 mL). Then, it was dried under vacuum, weighed, and stored for subsequent catalytic runs. The relevant catalytic tests are summarized in Table 25.

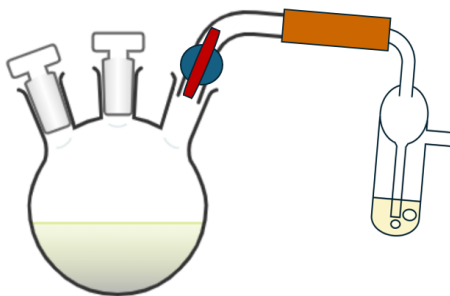


Fig. 58 - Experimental setup for the partial hydrogenation reaction of biodiesel using a Ni/calc-CA catalyst and NaBH_4 as a hydrogen source.

Table 25. Catalytic tests with Ni/calc-CA in biodiesel hydrogenation reaction using NaBH_4

Entry	T	t (min)	NaBH_4 (mmol)	Cat (mg)	18:0 (%wt)	18:2 (%wt)	18:1 (%wt)	CFPP < 10°C ^a	OS > 8h ^a	IV < 120g/100g ^a
1	RT	30	40	20	15,68	67,72	7,3	11,08	18,75	70,61
2	RT	20	40	20	15,13	64,47	11,1	10,21	13,21	74,38
3	RT	30	40	20	12,45	60,52	17,28	6,13	9,42	81,65
4	RT	30	25	15	8,15	59,08	23,19	-0,66	7,68	90,62
5	RT	30	30	15	11,33	64,82	14,61	4,23	10,66	80,73
6	RT	30	25	15	12,94	65,4	12	6,89	12,42	76,73

[a] - Key parameters biodiesel values according to REGULATION (EU) 2022/2383; the values in red do not fall within the limits set by European regulations.

Reaction conditions: a specific amount of catalyst were added to a solution of biodiesel (125 mg) in methanol (5.0 mL) with a suitable amount of NaBH_4 in a 25 mL three-necked round-bottom flask, equipped with a gas bubbler. The whole mixture was left under stirring at room temperature for the appropriate amount of time.

As reported in Table 25, among the various temperatures and NaBH_4 amounts tested, the optimized reaction conditions were found to be a reaction time of 30 minutes, 25 mmol of NaBH_4 , and 15 mg of Ni/calc-CA catalyst, conducted at room temperature (entry 6, Table 25). Under these conditions, the three key parameters—CFPP (Cold Filter Plugging Point), OS (Oxidation Stability), and IV (Iodine Value)—fell within the limits established by European regulations.

It was observed that the catalyst became magnetic after the first cycle of this reaction presumably due to formation of magnetic Ni nanoparticles.

4.10 Conclusion

In this study, the effectiveness of deep eutectic solvents in the purification of cigarette filters was demonstrated, with particular reference to the Choline Chloride:Levulinic Acid ($\text{ChCl}:\text{LevAc}$) system in a 1:3 molar ratio. This DES was distinguished by its ability to completely dissolve the cellulose acetate present in the filters, allowing subsequent precipitation and recovery of a pure, regenerated material. Spectroscopic (ATR-FT-IR, ^1H NMR) and thermogravimetric (TGA) analyses confirmed the effectiveness of the treatment, showing the complete removal of aromatic compounds and plasticizers.

The obtained material was subsequently used as a support for the synthesis of a nickel-based catalyst (Ni/calc-CA). A stable and efficient catalyst was obtained. Catalytic tests conducted in the partial hydrogenation reaction of FAMES showed promising activity of the Ni/calc-CA catalyst, returning encouraging preliminary results for obtaining an innovative catalyst that complies with circular economy principles. However, further testing is needed to optimize the reaction conditions and evaluate its recyclability. Therefore, it will be crucial to complete the study through the characteri-

zation of the catalyst to fully understand its behavior in catalysis and its unique properties. Calcination at 300°C altered the chemical nature of the support, rendering it a porous carbonaceous support needing further characterization. Therefore, it will be necessary to determine the composition and properties of the new support formed, which may have interesting properties.

Additionally, further research is planned to evaluate the performance of the calcined cigarette filters, both purified and non-purified, to verify whether they exhibit the same efficiency and if it is possible to completely remove the organic component. These aspects are crucial for better understanding the behavior and effectiveness of the catalyst. Future studies will address these questions and improve the understanding of the underlying mechanisms.

5 CONCLUSIONS

This research work addressed one of the most pressing and current challenges to which the scientific community dedicates its attention: finding innovative, concrete, and sustainable solutions to reduce environmental impact while simultaneously promoting the circular economy. Specifically, the focus was on the sustainable production of biodiesel using waste materials, starting from waste cooking oil as a raw material and employing waste such as steel slags, removed from open air disposal sites located near Taranto city (Italy), and cellulose acetate, extracted from used ciga-

rette filters, to produce catalysts useful for the process. In this way, a tangible contribution can be made to reducing greenhouse gas emissions and enhancing the value of materials otherwise destined for expensive disposal. Each chapter explored a specific aspect of this process, generating significant results that contribute to the advancement of biofuel research.

In the first chapter, the microwave-assisted transesterification reaction using steel slags as the catalyst was studied. This approach allowed for reducing energy consumption compared to traditional heating methods while ensuring a high yield in biodiesel production. Steel slags, being an industrial byproduct, represent a cost-effective and sustainable alternative to conventional catalysts. The results demonstrated that it is possible to successfully convert triglycerides of waste oils into fatty acid methyl esters (FAMEs), reducing the overall process costs and minimizing environmental impact.

In the second chapter, the focus shifted to optimizing the properties of biodiesel obtained from the transesterification of waste oil. The FAME mixture resulting from this reaction cannot be used as-is but requires improvement through a partial hydrogenation reaction, a crucial process for enhancing both oxidative stability and cold flow properties. Nickel-based catalysts supported on steel slags, Ni/Fe-SS and Ni/Fe-SSb, were synthesized and tested, demonstrating different catalytic activities using molecular hydrogen or NaBH_4 , as the reductant. The Ni/Fe-SS catalyst resulted more active than Ni/Fe-SSb since the more acidic support facilitated the partial hydrogenation reaction. The employing of these new catalysts led to a biodiesel with superior characteristics, making it more suitable for use in modern internal combustion engines. However, it emerged that the examined catalysts reduced their catalytic activity in subsequent reaction cycles, due to the increasing basicity of the supporting matrix.

The third chapter treated the synthesis and characterization of another new catalyst useful for upgrading biodiesel, composed of cellulose acetate extracted from

spent cigarette filters as support for nickel metal nanoparticles. In this framework, a novel purification method of cellulose acetate fiber was exploited by using Deep Eutectic Solvents, which replaced traditional solvents, due to their environmental sustainability and customizable properties depending on the eutectic mixture components. The most effective DES, which enabled the production of pure and reusable cellulose acetate (CA) was based on choline chloride and levulinic acid in a 1:3 molar ratio. The obtained CA was used as support of Ni nanoparticles, and the catalyst thus synthesized demonstrated high stability and catalytic activity in partial hydrogenation of FAMES using NaBH_4 as a reducing agent, confirming the possibility of using waste materials for reactions useful in biofuel synthesis. Further studies will be guaranteed to test the recyclability of the novel catalytic system.

Overall, the results of this thesis highlight how it is possible to create a biodiesel production process that is efficient, economical, and sustainable. The use of waste materials both as raw materials (waste oils) and as catalytic supports (steel slags and cellulose acetate) makes it possible to address environmental concerns related to waste disposal, transforming waste materials into valuable resources.

6 ACKNOWLEDGEMENTS

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SCIENTIFIC PUBLICATIONS

1. Leone, M. S., Mastroiilli, P., Mali, M., Porfido, C., Terzano, R., & Dell'Anna, M. M. (2023). *Waste Based Solutions for Preventing Water Pollution by Nitroarenes. 2023 IEEE International Workshop on Metrology for the Sea; Learning to Measure Sea Health Parameters, MetroSea 2023 - Proceedings*, 474–477.
2. Derobertis, F., Leone, M.S., Mesto, E., Schingaro, E., Porfido, C., Ditaranto, N., Mali, M., Dell'Anna, M.M., & Mastroiilli, P. (2024). *Microwave Assisted Biodiesel Production from Waste Cooking Oil Using Steel Slags as Catalyst. European Journal of Inorganic Chemistry*, 2024, 27, e202400375.



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