

Review

Fischer-Speier Esterification and Beyond: Recent Mechanistic Advances

Alberto Mannu *  and Andrea Mele 

Department of Chemistry, Materials, and Chemical Engineering “G. Natta”, Politecnico di Milano, 20131 Milano, Italy; andrea.mele@polimi.it

* Correspondence: alberto.mannu@polimi.it

Abstract: Over the past 130 years, Fischer-Speier esterification has been established as the benchmark method for synthesizing esters from organic acids and alcohols. The reaction’s versatility, arising from the vast combinations of starting materials and the numerous catalytic alternatives to the traditional H_2SO_4 , has maintained its relevance, with a steady flow of publications addressing new developments. This review highlights the most significant contributions to Fischer-Speier esterification over the past five years, with a particular emphasis on mechanistic advancements and innovative catalytic systems. Both homogeneous and heterogeneous catalytic approaches are discussed, including novel catalysts leveraging hydrogen-bonding interactions and systems offering fresh insights into specific reaction mechanisms and atypical methodologies. Some of these catalytic systems, as ionic liquids or sulfonated heterogeneous catalytic precursors, reached excellent yields (>90%), e.g., in the synthesis of fatty acids methyl esters. Also, classic catalysts such as H_2SO_4 and para-toluen sulfonic acid were optimized for quantitative conversions (e.g., in the esterification of trans-cinnamic acid with methanol). A consistent number of catalysts was studied with model substrates (as benzoic acid in combination with methanol, ethanol, and ethylene glycol), and new activation pathways were presented.

Keywords: Fischer-Speier esterification; ionic liquids; solid acid catalysis; esterification mechanism



Citation: Mannu, A.; Mele, A. Fischer-Speier Esterification and Beyond: Recent Mechanistic Advances. *Catalysts* **2024**, *14*, 931. <https://doi.org/10.3390/catal14120931>

Academic Editor: Jean-Marc Campagne

Received: 26 November 2024
Revised: 15 December 2024
Accepted: 16 December 2024
Published: 17 December 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In 1895, Emil Fischer and Arthur Speier published a research paper where they reported for the first time the esterification of several organic acids with absolute ethanol in the presence of reduced amount (<1 equivalent with respect to the organic acid) of mineral acids (HCl or H_2SO_4) [1]. As a matter of fact, they unlocked for the first time the catalytic mechanism of the esterification reaction in the presence of acids, allowing unthinkable (to date) optimizations and variations which have led the Fischer-Speier esterification to be the more employed protocol for ester’s production. The operational easiness related to the transformation has also led to the use of the protocol as a paradigm for teaching organic chemistry and catalysis principles to students [2,3]. Over the years, the number of combinations within acids and alcohols that can undergo Fischer-Speier esterification has grown exponentially, leading to a huge number of esters being exploited for industrial purposes. Esters play a crucial role in various industrial applications that significantly impact modern life. The transesterification of triglycerides with short-chain alcohols, such as methanol or ethanol, is a key process in the production of biofuels [4]. Additionally, the perfume industry extensively utilizes esterification reactions involving acids derived from natural sources to produce the main components of their formulations [5]. Large-scale production of esters also supports industries such as paints [6], plasticizers [7,8], pesticides [9,10], nutraceuticals [11], and food and cosmetics [12]. Also, fuel additives as esters of levulinic acid have been reported to be of industrial interest [13].

The topic in broader meaning was reviewed by Khan and coworkers in 2021 [14]. The Authors published a comprehensive review of the state of the art in esterification, discussing the Fischer-Speier protocol but also enzymatic and thermal noncatalytic esterification.

Despite its large success in synthetic organic chemistry and the elevated number of papers dealing with the optimization of such reaction, the presence of multiple equilibria leading to moderate yields has limited its application, pushing the search for alternative and more efficient protocols as the Steglich reaction [15].

Nevertheless, the simplicity and the wide applicability of the Fischer-Speier esterification can't be reached by any other known chemical transformation for esters, making this route the one of choice even in current days for many syntheses. Also, the understanding of possible deactivation pathways by analyzing the literature data can lead to new ideas to improve the reaction. The affirmation during the year of the Fischer-Speier esterification was also due to the discovery of new catalytic systems, both homogeneous and heterogeneous. New combinations of reagents and catalysts are continuously reported, and variations from the original mechanism are presented and discussed.

In this context, the present review is focused on the recent advances of the Fischer-Speier esterification, covering the papers published during the last five years. The following procedure was adopted to collect the papers of interest from the Scopus database: period—2020–2024, document type—article or review, language—English. Thus, of the 88 documents selected, the ones showing any discussion about the Fischer-Speier esterification have been herein reported, with a particular focus on any reporting about mechanistic advancements. A particular focus is given to the reaction conditions and to the outcomes in relationship with the specific substrates and catalysts, highlighting any possible activating and deactivating pathways and proofs of concept of new mechanisms. The reason for such an approach lies in the existing gap between the industrial employed protocols and the advancements reported at the laboratory level. When a protocol that involves many equilibria and the generation of side-products able to inhibit the advancement of the transformation (as water in this case) is scaled at the industrial level, many issues arise as a consequence of the accumulation of unreactive or detrimental species. In this context, excellent conversion or yield at the laboratory scale does not guarantee the same level of effectiveness in the scaled protocol. Under this light, the importance of the understanding of the mechanism and the knowledge about any possible species involved became pivotal.

The review is organized in two parts. Section 2.1 provides a general description of the reaction, including a summary of the classic mechanism and intermediate species involved. Section 2.2 deals with the analysis of the selected bibliography, highlighting their mechanistic contributions to the ester's synthesis and to the development of the protocol. Section 2.2 is, in turn, divided into two main parts: the first one is dedicated to the homogeneous systems, while the second one regards the heterogeneous ones. The main aim of the present review paper was to collect any contribution dealing with the Fischer esterification published during the reported period and provide information about the mechanism of the esterification described.

2. The Fischer-Speier Esterification: Basic Aspects

The Fischer-Speier reaction is an esterification between an organic acid and an alcohol catalyzed by Brønsted–Lowry or Lewis acids. The mechanism of the reaction is known and widely accepted. At first, the catalyst activates the carbonyl group, making it suitable for attack by a weak nucleophile as an alcohol. After the alcohol addition, one molecule of water is produced and eliminated to provide the ester after the decoordination of the catalyst (Figure 1).

Despite an apparent simple mechanism, the Fischer-Speier esterification is a complex combination of equilibria, each one influenced by the specific molecules involved. The key steps are the activation of the carbonyl moiety (step I), which can occur in principle with any kind of Lewis acid, and the water elimination (step III), which directly influences the yield of the esterification. Overall, the thermodynamics of the equilibria depicted in

Figure 1 determines the result of the reaction. At the end, one C(carbonyl)-O bond is broken, and one C(carbonyl)-O bond is formed, making de facto the reaction an acyl nucleophilic substitution. The eventual water presence in the reaction medium strongly deactivates the formation of the ester. This behavior is exploited in the acid-catalyzed hydrolysis of the esters, which is a reverse Fischer-Speier esterification [16].

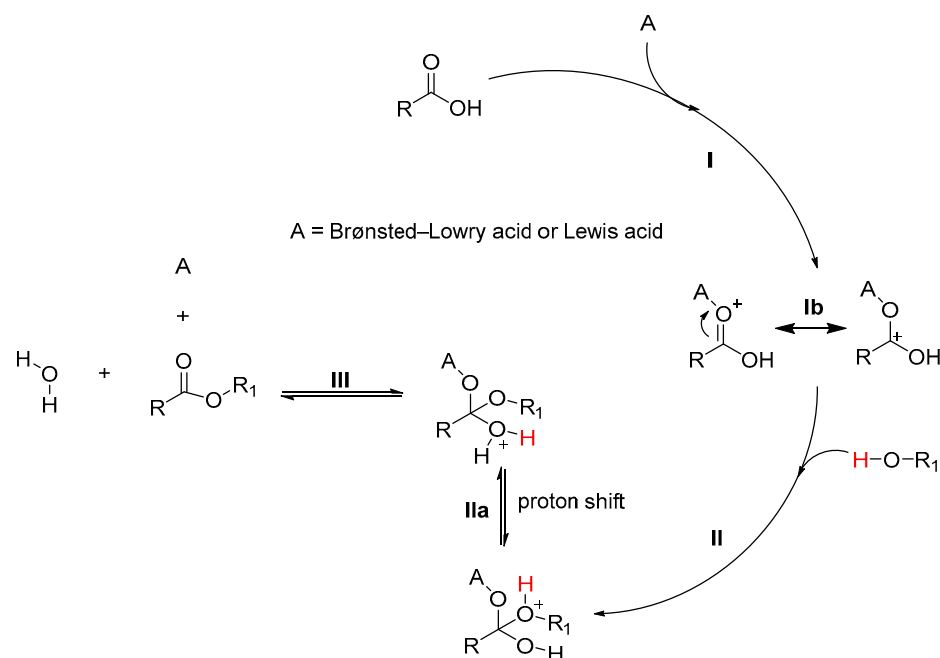


Figure 1. General mechanism of the Fischer-Speier esterification.

2.1. Overview of the Recent Advances

During the last five years, the number of papers involving at least one reaction based on acid-catalyzed esterification was consistent and related to different catalytic systems. A compressive list of the main studies from 2020 reported in the literature, which employ Brønsted or Lewis catalysts, is reported in Table 1.

Table 1. Recent papers dealing with Fischer-Speier esterification. Substrates, catalysts, and references are reported.

Acid	Alcohol	Bronsted Catalyst	Reference
formic acid, acetic acid, salicylic acid, benzoic acid	2-propanol, ethanol, isobutanol	H ₂ SO ₄	Altalhi et al. [17]
peptide aCT11	methanol	HCl	Bannon et al. [18]
acetic acid	vanillyl alcohol	H ₂ SO ₄	Jayawijayanti et al. [19]
4-Amino-3-nitrobenzoic Acid	methanol	H ₂ SO ₄	Kam et al. [3]
lactic and butyric acids	chitin	HCl	Magnani et a. [20]
acetic acid	cellulose	H ₂ SO ₄	Luis et al. [21]
trans-cinnamic acid	methanol	H ₂ SO ₄ or pTSA	Steele et al. [2]
eleostearic acid	polyether alkynyl alcohol	p-toluenesulfonic acid	Song et al. [22]
amino acids (L-Alanine, L-phenylalanine, L-tyrosine, L-lysine, and L-glutamic acid)	methanol	H ₂ SO ₄	Salvitti et al. [23]
1-methyl-3-indoleacetic acid, benzofuran, naphthalene, thiophene, pyridine, substituted benzenes, formate derivatives, D-(−)-tartaric acid, several natural and unnatural amino acids (alanine, valine, leucine, isoleucine, proline, threonine, serotonin, tyrosine.	methanol, ethanol, i-propanol, t-butanol, cyclohexanol, ethylene glycol, 1,3-propanediol, triethylamine alcohol, glycerol	B(C ₆ F ₅) ₃	Ya-Lan et al. [24]

Table 1. Cont.

Acid	Alcohol	Bronsted Catalyst	Reference
acetic acid	n-pentanol	sulfated zirconia	Hamerski et al. [25]
Free Fatty Acids (FFAs) from vegetable oils	methanol	BF ₃ or AlCl ₃	Kolet et al. [26]
palm fatty acid	methanol	Al ₂ (SO ₄) ₃ or H ₂ SO ₄ ¹	Ulfah et al. [27]
Acid	Alcohol	Lewis Catalyst	Reference
polyacrylic acid	SiOH	SnCl ₂	Ranno et al. [28]
acetic, propionic, butyric, octanoic, hexanoic, adipic, suberic, linoleic, oleic, caprylic, ricinoleic	isosorbide, isomannide	Amberlyst-15	Städtke et al. [29]
2-(((2-ethylhexyl)oxy)carbonyl)benzoic acid	2-ethylhexanol.	mixed Sn/Ti catalysts	Jansen et al. [30]
propane-1,2,3-tricarboxylic acid	n-propanol	Al ₂ (SO ₄) ₃	De Bruyne et al. [31]
glacial acetic acid	n-pentanol	piperazine-based acid molten salt	Zaharani et al. [32]
oleic acid	methanol	biochar from murumuru kernel shells	Correa et al. [33]
tall oil fatty acids	methanol	Amberlyst® BD20 or H ₂ SO ₄	Lawer-Yolar et al. [34]
linoleic acid	methanol	HZSM-5 zeolites	Fawaz et al. [35]
nonanoic acid	2-ethylhexanol	Amberlite IR120	Russo et al. [36]
acetic acid	isoamyl alcohol	Amberlyst 15 dry, Amberlyst 16 wet, Amberlite 120-IR	Zare et al. [37]
benzoic acid	methanol	Bronsted acidic ionic liquids	Bano et al. [38]
oleic acid	methanol	SO ₃ H-PPAC (from ZnCl ₂)	Hussein et al. [39]
oleic acid	methanol	[N,N-di(propanesulfonic)phenylenediamine][ethanol] ₂	Xiao et al. [40]
oil fatty acid	ethanol	Zr ⁴⁺ -CER	Zhu et al. [41]
oleic acid	methanol	S150-4	Zhang et al. [42]
acetic acid	n-butanol	Propyl-SO ₃ H functionalized graphene oxide	Masteri-Farahani et al. [43]
palmitic acid	ethanol	Bronsted acidic ionic liquids	Chandrika et al. [44]
3-mercaptopropionic acid	9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene	para-toluensulfonic acid	Hong et al. [45]
rosin acid	starch nanoparticles	Maghnite-H+	Bezzekhami et al. [46]
glacial acetic acid	1-butanol	4,4'-trimethylenedipiperidinium hydrogen sulfate hydrate	Zaharani et al. [47]
acetic acid	aminotriphenols	titanium aminotriphenolate	Wolzak et al. [48]
Butyric, caproic, pelargonic, oleic, linoleic, levulinic acid	1-hexanol, 2-ethylhexanol, 1-hexadecanol	ZnCl ₂ , ZnCO ₃ , Zn(OAc) ₂ , ZnO, Zn(ClO ₄) ₂ , Zn(TfO) ₂ , and Zn(BF ₄) ₂	Melchiorre et al. [49]
benzoic acid	ethylene glycol	bisimidazolium tungstates	Wu et al. [50]
levulinic acid	ethanol, n-butanol, n-exanol	dendritic fibrous nano-silica derivate	Alsalm et al. [51]
levulinic acid	cydecanol formed in situ from dicyclopentadiene	Amberlist resin	Chung et al. [52]
oleic acid	methanol	[N,N-di (propanesulfonic) phenylenediamine][ethanol] ₂	Xiao et al. [40]

¹ Both Bronsted and Lewis acids were used in this publication.

To describe and summarize the advancements recently achieved (2020–2024), a classification of these studies based on the nature of the catalyst with respect to the substrates is proposed. In Section 2.2, the Fischer-Speier esterification in homogeneous systems is described, while Section 2.3 deals with the employment of heterogeneous systems.

2.2. Fischer-Speier Esterification Promoted by Homogeneous Catalysts

2.2.1. Bronsted Acids as Catalysts

Regarding the homogeneous systems, formic, acetic, salicylic, benzoic (with 2-propanol, ethanol, isobutanol) [17], acetic (with vanillyl alcohol [19] or cellulose [21]) 4-Amino-3-nitrobenzoic (with methanol) [3], cinnamic (with methanol) [2], palm acids (with methanol [27]) and amino acids as L-Alanine, L-phenylalanine, L-tyrosine, L-lysine, and L-glutamic acid (with methanol) [23] were activated with the classic Bronsted acid H₂SO₄.

catalyst was not random. In fact, HCl dissociation was exploited to hydrolyze part of the glycosidic linkages of the chitin while catalyzing the esterification between the acid and the hydroxyl groups of the chitin, thus completing a tandem hydrolysis/esterification process. The yields reported by the Authors range between 40% and 60% [20].

2.2.2. Acidic Ionic Liquids

During the last few years, acidic ionic liquids have been tested as catalysts for Fischer-Speier esterification, opening a different concept of catalysis: the activation of substrates through hydrogen-bonding interactions. Despite the difficult implementation of ionic liquids in industrial productions due to their general toxicity and the high price of components, their application on a laboratory scale as catalysts for the Fischer-Speier esterification is of high interest. The possibility to activate the carbonyl or the alcohols by a sort of Lewis catalysis operated by an intense hydrogen network represents a novel protocol at its early stages of development.

In this context, Xiao and coworkers presented the possibility of promoting the esterification of oleic acid with methanol by using as a catalyst the system $[N,N$ -di (propanesulfonic) phenylenediamine][ethanol]₂. The Authors discussed some mechanistic aspects regarding the molecular structure of the catalyst. Being the catalyst composed of a mixture of hydrogen bond acceptors and donors, its activity is strictly related to the intensity and extension of the hydrogen bond network. Thus, to obtain suitable levels of acidity, the solvent used for the preparation of the mixture between the N,N -di(propanesulfonic) phenylenediamine (hydrogen bond acceptor) and the ethanol (hydrogen bond donor) resulted pivotal, with ethanol being the best reaction medium. Optimized conditions, which consisted of 3 wt% of catalyst, with a methanol/oleic acid ratio of 10:1 and 70 °C, allowed to reach more than 96% of conversion after 1.5 h [40].

Bronsted acid ionic liquids catalysts made by pyridinium $[PyH]^+$ and triethylammonium $[TEAH]^+$ were used by Bano and coworkers for the esterification of aromatic acid with different aliphatic alcohols (Figure 3) [38].

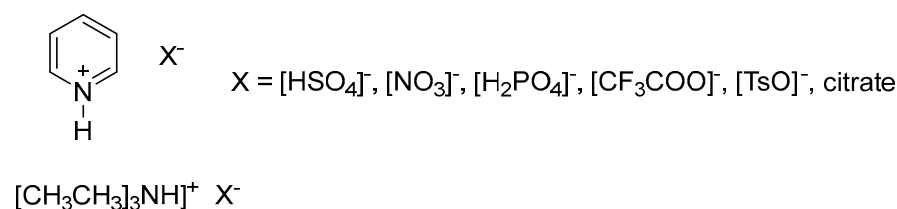


Figure 3. Bronsted acid Ionic liquids catalyst reported by Bano et al. [38].

Starting from the model esterification between benzoic acid and methanol, the Authors tested the catalysts reported in Figure 3 and determined the best reaction conditions (benzoic acid 1.69 mmol: methanol 4.2 mmol, cat. 0.42 mmol, 70 °C for 16 h). The reaction was then extended to different benzoic acid derivatives and aliphatic alcohols. Some trends were then encountered. Looking at the catalysts, considering different anions, a decreasing catalytic activity was observed in the following order: $[\text{HSO}_4]^- > [\text{H}_2\text{PO}_4]^- > [\text{OTs}]^- > [\text{citrate}]^- > [\text{NO}_3]^-$. Considering the effect of the nature of the acid on the outcome of the reaction, an increase in the catalytic activity was observed as more electron-withdrawing groups were present on the benzoic acid. A mechanism was then proposed for the esterification of such conditions (Figure 4).

In this case, the acidity of the $[\text{HSO}_4]^-$, as well as the basicity of the $[\text{SO}_4]^{2-}$ anions, were pivotal, respectively, in activating the benzoic acid and in re-establishing the carbonyl moiety in the corresponding ester, favoring its production (Figure 4).

A similar study was conducted by Wu and coworkers with the same acid (benzoic) and ethylene glycol using basic ionic liquids of bisimidazolium tungstates [50]. Also, in this case, the effect of different anions was assessed. The point of major interest was represented by the basic nature of the catalysts, which can't generate any proton to activate

the carboxylic function as expected in Fischer-Speier esterification. Nevertheless, the high capacity of the anion of ionic liquids to form hydrogen bonds with the carboxylic acid and the alcohol was indicated as the activating steps of the catalytic cycle. Also, the capacity of WO_4^{2-} to activate short chains of alcohol as ethanol was recently documented [55]. The Authors proposed a mechanism according to Figure 5 [50].

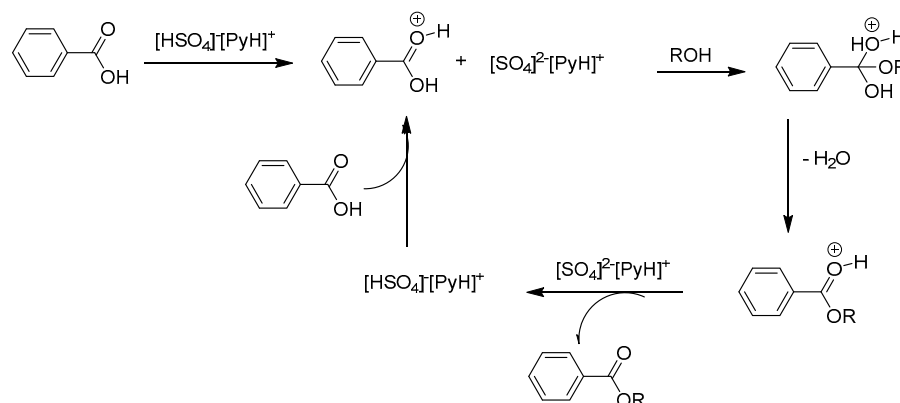


Figure 4. Mechanism of the esterification between benzoic acid (and derivatives) with aliphatic alcohols catalyzed by pyridinium-based ionic liquids [38].

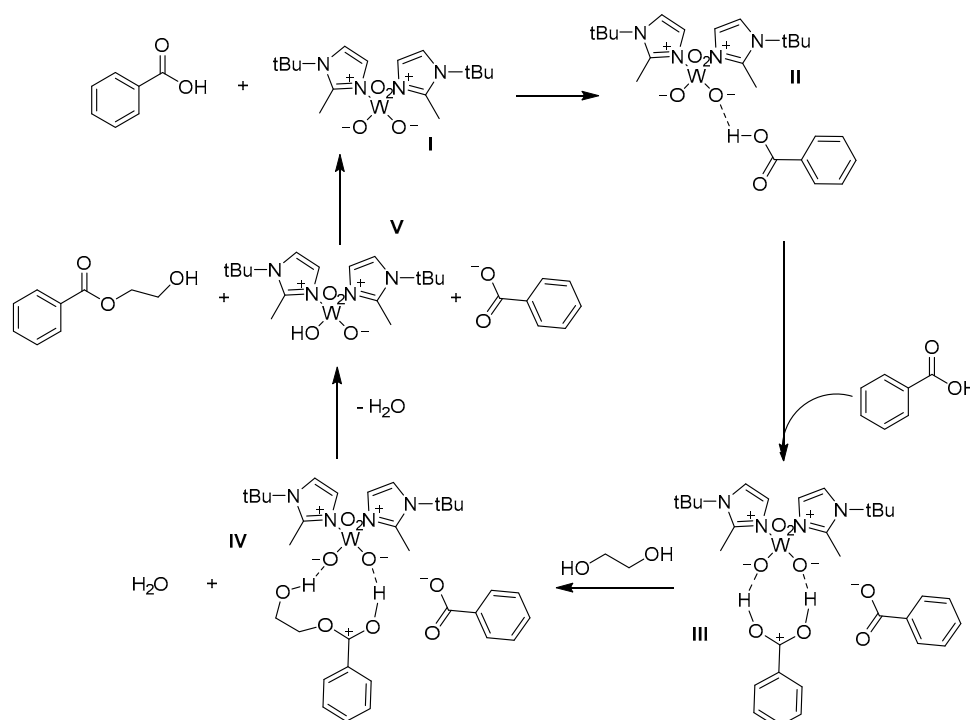


Figure 5. Mechanism proposal about the esterification of benzoic acid and ethylene glycol catalyzed by bisimidazolium tungstates [50].

According to the mechanism reported in Figure 5, in this case, the activation of the carboxylic acid occurs as a consequence of the coordination of the acidic proton of the benzoic acid to the catalyst to form the intermediate species II. Insertion of a second molecule of acid and decooordination of a carboxylate produces intermediate III. A nucleophilic attack by the oxygen of the alcohol to the activated carbonyl carbon promotes the generation of H_2O and the ester formation (IV), recovered after decooordination from the metal with the concomitant restoring of the catalyst (Figure 5).

Kinetic studies were conducted by Chandrika and coworkers [44] with similar ionic liquid catalysts for the esterification of palmitic acid with ethanol (150 °C for 15 min). The

Authors indicated the protonation of the acid by the catalyst as the rate-determining steps, in accordance with the mechanism reported in Figure 3 by Bano et al. [38]) and calculated the main kinetic parameters for the specific systems considered [44].

2.2.3. Lewis Acids as Catalysts

Despite the intensive research conducted during the last 50 years about the activation of carbonyl moiety by Lewis acids, this specific topic was one of the most reported in recent literature.

Ya-Lan et al. [24] reported in high yields the chemo- and site-selective mono-esterification of glycerol with different acids in the presence of $B(C_6F_5)_3$ [24]. The synthetic protocol was developed on the condensation of the 1-methyl-3-indoleacetic acid with methanol, taking into consideration different catalysts and solvents. The catalyst $B(C_6F_5)_3$ under optimized conditions was then tested in a wide substrate scope, including different acids and alcohols (see Table 1). To highlight the chemo-selectivity with glycerol, which provided the monoester with high yields (83%), which resulted in consistently influenced by the solvent used, with tetrahydrofuran (THF) being the best one. No further mechanistic studies were reported.

The acidic esterification of fatty acids was one of the most studied topics during the last five years. Melchiorre and coworkers [49] conducted a comprehensive study about the ability of different zinc salts to promote condensation between several fatty acids and alcohols. Of particular interest is the comparison between the catalytic activity of the catalysts $ZnCl_2$, $ZnCO_3$, $Zn(OAc)_2$, ZnO , $Zn(ClO_4)_2$, $Zn(TfO)_2$, and $Zn(BF_4)_2$ which differ for the anion. Considering the esterification between the pelargonic acid (PA) and the 2-ethylhexyl alcohol (20% in excess) under reflux conditions, the corresponding ester was obtained in yields ranging from 85% (for $Zn(BF_4)_2$) and 99% (for $Zn(ClO_4)_2$ and $Zn(CF_3SO_3)_2$). A trend related to the Bronsted basicity was observed in the catalytic activity, which followed the order for $Zn(BF_4)_2 < ZnCl_2 < ZnCO_3 = ZnO < Zn(OAc)_2 < Zn(ClO_4)_2, Zn(TfO)_2$. A side reaction was reported for the zinc oxide, which led to the formation of zinc pelargolate, which precipitates in solid form from the reaction mixture. This behavior was not observed with zinc perchlorate and zinc triflate.

Also, the different solubility of these zinc salts was exploited to recover the catalyst at the end of the reaction. In this context, zinc perchlorate and zinc triflate, although more active, were not the best candidates for a recycling procedure. On the other hand, with zinc oxide, which is soluble in the reaction conditions (up to 100 °C) but not at r.t., no lowering of the yield was observed even after five recycling cycles. Regarding the nature of the catalytic species, it resulted in being composed of zinc carboxylate, formed during the first cycle and then persistent during the recycling cycles [49].

Coming back to the reaction mechanism, Wolzak and coworkers [48] reported a study about the catalytic activity of $Ti(OiPr)_4$ and different Ti-aminotriphenol complexes in the esterification of benzoic acid and heptanol (1/10 ratio). It was found that the catalyst coordinates both a carboxylate and a carboxylic acid in the resting state and that at the end of the catalytic cycle, one alkoxide is coordinated to the metal complex. The Authors integrated this evidence with DFT studies and proposed a detailed mechanism for the reaction where the interaction between the oxygens of the aminophenol ligand interacts with the O-H of the intermediate species, pushing the reaction toward the products (Figure 6) [48].

Catalytic precursor I coordinates two molecules of benzoic acid in two different ways (the first through the carbonylic oxygen and the second through the -OH oxygen) to form active catalytic species II. In this case, the nucleophilic oxygen of the carbonyl coordinated by the oxydrilic part can attack the -OH function of the alcohol, which, in turn, performs a nucleophilic attack to the positively charged carbon of the acid coordinated through the carbonyl moiety (IV). Then, water is produced and eliminated, which promotes the generation of the corresponding ester (V), Figure 6.

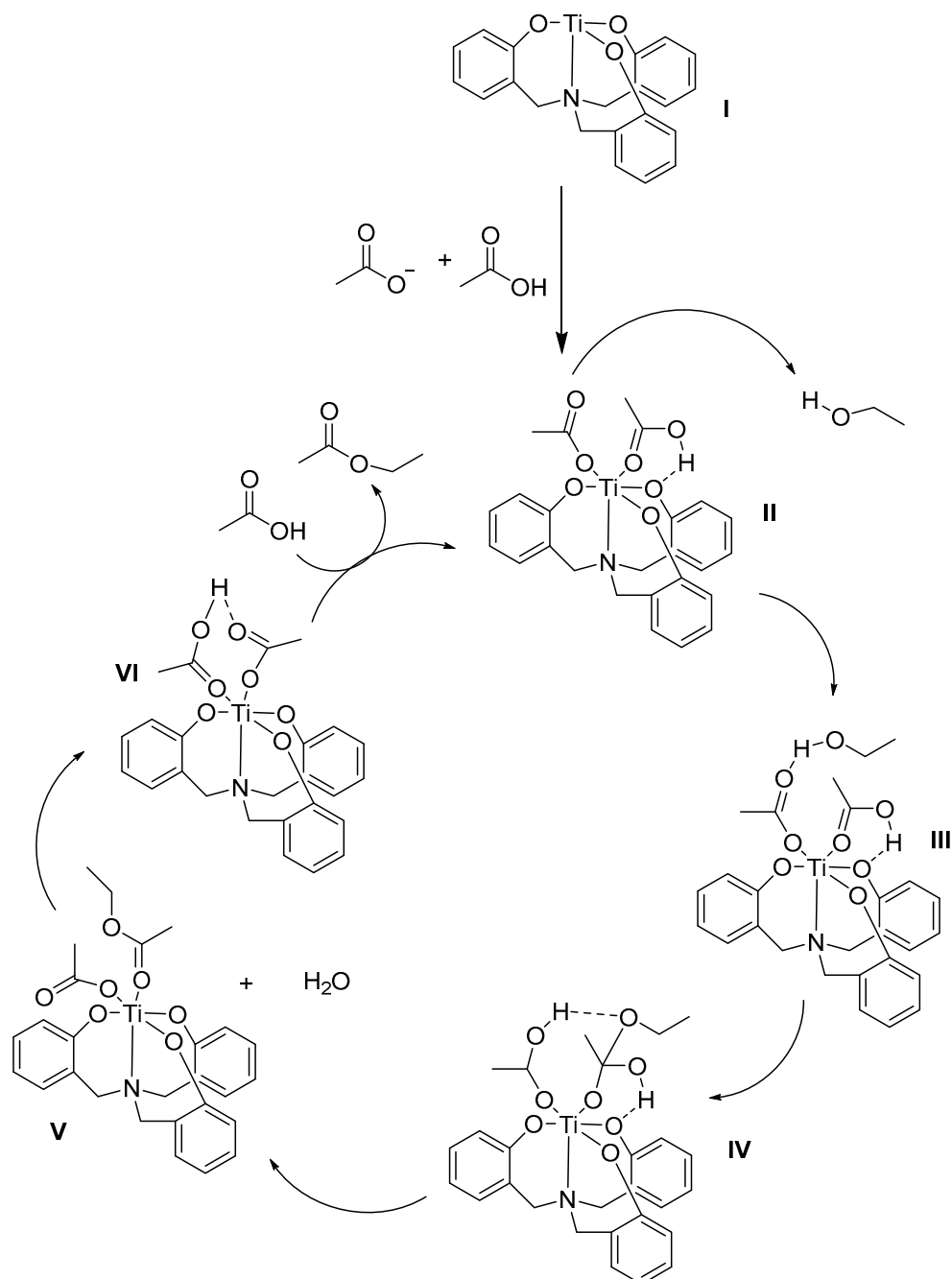


Figure 6. Esterification of acetic acid with ethanol catalyzed by Ti-amino triphenol complex, according to Wolzak et al. [48].

Moving to molten salts, Zaharani and coworkers [32] tested the salt 4*H*,4*H'*-trimethylenedipiperidine-dium hydrogen sulfate hydrate, $[\text{TMDPH}_2]_2 + 2[\text{HSO}_4]^- \times \text{H}_2\text{O}$, as a catalyst for the esterification of acetic acid with different alcohols obtaining good results (yields between 73% and 82%). Working in two-phase conditions (cyclohexane and acetic acid), continuous extraction of the esters was achieved during the advancement of the reaction, shifting the equilibrium toward the product. Also, the Authors claimed an effect of the hydrogen bond network existing in the catalyst structure in activating the alcohol by enhancing its nucleophilicity [32].

Luis et al. [21] reported the successful acetylation of cellulose by Fischer-Speier esterification in the presence of acetic anhydride. The driving force behind the activation of the -OH groups of the cellulosic biomass was the dissolution of the cellulose in the ionic liquid

AMIM Cl (1-methylimidazol and allyl chloride in a molar ratio of 1 to 2). The protocol resulted successfully in obtaining values of dm (degree of modification) comparable with the analog commercial acetyl cellulose (dm = 0.58).

Also, SnCl_2 was successfully used to promote the esterification of polyacrylic acid with the silanol groups of the SiO_2 surface of crown ether-decorated silicon photonic sensors for Pb^{2+} detection [28].

Also, $\text{Al}_2(\text{SO}_4)_3$ was effective as a catalyst for the esterification of *n*-butanol, providing the corresponding ester in 90% of yield [31]. On the other hand, magnesium aluminum layered double hydroxide was effective in catalyzing the esterification of the lactic acid with ethanol.

Jansen and coworkers [30] studied the employment of heterobimetallic carboxylate Ti/Sn dimers as catalysts for the esterification of the monoester derived from the phthalic anhydride and 2-ethylhexanol. A consistent spectroscopical investigation, including UV-VIS and NMR analysis, was carried out to detect intermediate species and determine the nature of the catalytic activity. Comparing the performances of the mixed complex with the ones of the two Ti and Sn dicarboxylate complexes, a decreased deactivation of the catalyst was observed by *ex situ* UV-VIS in the case of the bimetallic one. The robustness of the catalyst was justified by the reduced accessibility of the water in higher coordination metal clusters, which prevented hydrolysis side-reaction. Also, taking into consideration the ability of distannoxanes to exploit the presence of close metals to properly coordinate the reagents in the formation of intermediate species, a kind of assistance to the Sn by the adjacent Ti was hypothesized. Thus, the following mechanism was proposed (Figure 7).

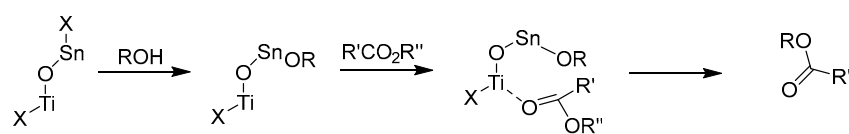


Figure 7. Proposed mechanism for the Fischer-Speier esterification mediated by heterobimetallic Ti/Sn complexes [30].

2.3. Fischer-Speier Esterification Promoted by Heterogeneous Catalysts

Even in the last years, the interest in the employment of solid acid catalysts for promoting Fischer-Speier esterification was high. Looking at the literature, three main categories of papers can be encountered: proposal of new catalysts, screening of already reported catalysts with a new combination of substrates, and reporting of additional data about already known systems.

In this context, Hamerski and coworkers [25] reported a kinetic study about the esterification of acetic acid with *n*-pentanol in the presence of the sulphated zirconia solid catalyst ($\text{SO}_4\text{-ZrO}_2$). The Authors considered three models (pseudo-homogeneous, Langmuir-Hinshelwood, and Eley-Rideal) for their study (Table 2).

Table 2. Mechanisms considered for the esterification of acetic acid with *n*-pentanol with sulfated zirconia [25].

Model	Mechanism
PH	Pseudo-homogeneous
LH_AD_P	Langmuir-Hinshelwood, adsorbed acetic acid reacts with adsorbed <i>n</i> -pentanol
ER_AC_ADS	Eley-Rideal, adsorbed acetic acid reacts with <i>n</i> -pentanol in the liquid phase
ER_P_ADS	Eley-Rideal, adsorbed <i>n</i> -pentanol reacts with acetic acid in the liquid phase

In the temperature range between 50 °C and 80 °C, a statistically relevant influence of the interaction between the reagents and the active acid sites of the catalyst ruled out the PH mechanism, while LH and ER models were both feasible. Of particular interest was the discovered interaction of water with the active sites of the catalyst, which was higher than the one of the acetic acid, with an inverse proportion with respect to the temperature.

Considering that the reaction proceeds through the adsorption of the acid into the acidic sites of the catalyst (Zn^{2+} and H^{+}), followed by the nucleophilic attack of the alcohol on the acid, competition with water takes place on the active sites of the catalyst. Thus, reducing the temperature is possible to increase the conversion by reducing the affinity of the water for the acidic sites of the catalyst [25].

A relevant amount of research efforts has been dedicated to the application of Fischer-Speier esterification to produce biofuels and, in particular, fatty acids methyl esters. Kolet et al. [26] studied the application of BF_3 and $AlCl_3$ to the esterification of the oleic acid with methanol under sol-gel conditions. The catalytic species, after immobilization on silica and ultrasonic activation, were individuated in B_2O_3 and $AlCl_3 \times 6H_2O$, respectively. Regarding the mechanistic aspects, a detrimental effect of water was observed, in part resolved through drying the starting materials, but still relevant in the case of the hydrated form of $AlCl_3$. A similar reaction was explored by Fawaz and coworkers [25], who reported the esterification of linoleic acid with methanol over HZSM-5 zeolites. In this case, a relationship between the catalytic outcome and the composition of the zeolite was found. Considering three variants of the catalyst, which differed for the Si/Al ratio (53, 33.3, 14.4), in the first 2 h of the reaction, an expected increase of the catalytic activity was observed for catalysts with a reduced Si/Al ratio (having more Bronsted acidic active sites). Nevertheless, after 4 h of reaction, a decreasing conversion was observed in the case of the catalyst with a Si/Al ratio of 14.4. Even in this case, a competition between the water formed during the first part of the reaction and the reagents was indicated as pivotal in determining the outcome of the reaction. Thus, the hydrophobicity of the catalyst should also be considered along with the Bronsted acidity [35].

The esterification of fatty acids by acidic solid catalysts has been extensively studied recently [33]. da Luz Correa et al. developed a catalyst based on sulfonated biochar of waste origin, which was tested on the esterification of oleic acid with methanol. The Authors reported 97.2% conversion at 90 °C for 4 h in the presence of 5% of catalyst and with a 10/1 methanol/oleic acid ratio. Regarding the mechanism proposed, the acid-base reaction through the $-SO_3H$ group of the catalyst and the carboxylic group $-COOH$, which generated the carboxylate COO^- anion, was indicated as the activation step. Then, the carboxylate could interact through hydrogen bonding with the $-O-H$ function of the alcohol, enhancing its nucleophilicity and thus promoting esterification. The possibility of reusing for multiple cycles the catalyst was also explored, and a potential leaching of part of the catalyst was observed after four cycles [33].

The same reaction with a similar catalyst was explored by Hussein and coworkers [39] (97% yield at 80 °C for 2.5 h in the presence of 5% of catalyst). The catalyst was derived by the sulfonation of porous carbon obtained by peel waste. Recyclability studies were also carried out, which indicated a consistent drop in the catalytic activity from the fifth cycle. Unfortunately, the catalysts undergo gradual leaching, which consistently lowers the catalytic activity after a few cycles. The Authors reported as efficient the sulfonation of the catalyst prior to its reuse. Comparison of the same reaction without a catalyst in the presence of a non-sulfonated version of the catalyst confirmed the relevant role of the $-SO_3H$ group in promoting the reaction. Differently from the proposal of Correa et al. [33], in this case, a classic mechanism was proposed, both the mechanisms are reported in Figure 8.

Looking at different solid acid catalysts for the same type of substrates, to notice the employment of sulphated alumina [27], of a Zr_4^+ CER resin [41], the use of a carbon-based S150-4 catalyst [42], and the testing of a mixture between Amberlyst® BD20 and Ambersep BD 19 [34].

Städke et al. [29] studied the esterification of bio-based diols isosorbide and isomannide with different short-chain organic acids mediated by Amberlist 15. A drastic decrease in the conversion and selectivity was observed in multiple cycles of catalysis after the first run for the reaction between isosorbide and acetic acid. Physicochemical analysis, including SEM, elemental analysis, and N_2 -physisorption of the catalyst before and after the first

catalysis, suggested the presence of leaching of the acidic sites of the catalyst, responsible for the drop in conversion.

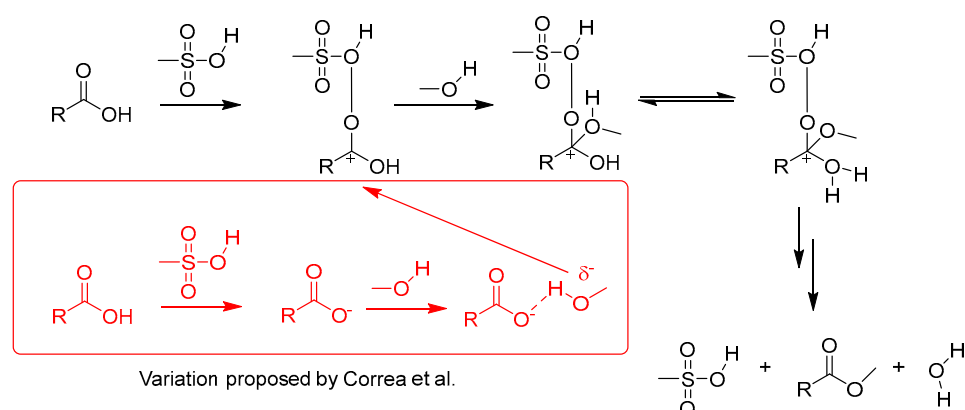


Figure 8. Comparison between the mechanism proposed by Hussein [39] integrated with the variation suggested by Correa et al. highlighted in red color [33].

Employing Amberlist resins as a catalyst in the presence of levulinic acid and cyclopentadiene, Chung and coworkers [52] observed the in situ formation of the cycdecanol (corresponding alcohol from the reduction of the endocyclic C=C bond of the cyclopentadiene) and the subsequent Fischer-Speier esterification. The Authors discussed the formation of cycdecanol, which can be formed in the presence of the water of hydration of the Amberlist. Also, a further supply of water during the advancement of the esterification can be guaranteed by the esterification itself, which produces H₂O as a byproduct.

Ulfah and coworkers [27] reported a comparison between the homogeneous H₂SO₄-catalysed esterification of a palm fatty acid distilled with methanol and the same reaction activated by sulphated alumina (12 wt%). The Authors considered different parameters such as the alcohol/acid ratio, the catalyst loading, and the reaction time. For the heterogeneous reaction, an ideal fatty acids/methanol ratio of 1 to 1.7 was reported, and a plateau for the conversion at higher methanol concentrations was observed. Regarding the catalyst, a decrease in the conversion was reported for the increased amount of sulphated alumina (84% for 12 wt% of catalyst, 80% for 20 wt%, and about 78% for 28 wt%). Considering the heterogeneous nature of the system, the Authors addressed this behavior to a limited mass transfer capacity when more than 12 wt% of catalyst was used.

On the other side, the homogeneous esterification showed quantitative conversions when the amount of H₂SO₄ was fixed at 7.4 wt% (with respect to the acid), while the ideal acid/methanol ratio resulted in 1 to 1.5. Finally, the best reaction time was indicated as 3 h [27].

Zhu and coworkers [41] subjected to esterification Tall oil fatty acids (TOFA) to esterification with methanol in a fixed bed membrane reactor in the presence of the acid catalyst Zr₄⁺CER. Operating with an ethanol/oil molar ratio of 15:1 at 80 °C in a catalytic bed height of 120 mm with a feeding rate of 0.3 mL per min., conversions >99% were achieved. Also, the catalysts were highly recyclable, showing a minimal decrease in the catalytic activity after six cycles (90%). The same reaction and substrates were studied by Lawer-Yolar and coworkers, using the catalyst obtained by combining Amberlyst[®] BD20 and Ambersep BD 19 [34]. Also, in this case, yields > 90% were obtained after just 60 min at 55 °C and with a catalyst concentration of 0.5 wt% and 1/15 oil/alcohol mass ratio. A Design of Experiments approach combined with multivariate analysis was employed to assess the effect of the main parameters and their combination on the outcome of the esterification and to determine the ideal conditions. Also, recyclability studies were conducted, which showed good conversions, close to 90%, after four recycling cycles.

Quantitative yields were also reported by Zhang and coworkers [42] after 8 h of esterification of oleic acid and methanol at 65 °C, with a catalyst loading of 10 wt% and an alcohol/acid ratio of 8/1. A consistent characterization of the catalyst (S-150-4), ob-

tained from the sulfonation with H_2SO_4 of powdered bamboo followed by carbonization, was conducted.

A different sulfonated acidic solid catalyst (graphene-based acid catalyst, $\text{GO-PrSO}_3\text{H}$) was also studied by Masteri-Farahani and coworkers [43], who described the esterification of oleic acid and acetic acid, respectively, with *n*-butanol and methanol. Acetic acid was easily converted in high yields, while oleic acid shows, in the condition employed (80 °C, acid/alcohol ratio 1/10, 5 wt% of catalyst), moderate yields (60%).

Esterification of levulinic acid with *n*-butanol or *n*-hexanol was achieved through catalysis mediated by dendritic fibrous nano-silica decorated with sulfonic acid functional groups by Alsalim and coworkers [51]. According to the Authors, a first protonation on the carboxylic acid by the sulphonate groups of the catalyst started the reaction, followed by the nucleophilic attack of the alcohol on the activated carbonyl. According to the classic mechanism, tautomerism produced one molecule of H_2O , which was then eliminated, while the deprotonation of the activated carbonyl by the SO_3^- group of the catalyst restored the sulphonate starting group.

Russo and coworkers [36] studied the kinetics of the esterification of nonanoic acid with 2-ethylhexanol in the presence of the acidic solid catalyst Amberlite IR120 in comparison with the homogeneous H_2SO_4 catalysed process. The two processes resulted in having the same activation energy and the same mechanism. Nevertheless, a significant induction period independent of the fluid-solid mass transfer was reported. Kinetic studies suggested a change of the particle radius during the reaction, which was explained by the swelling of the Amberlist in the presence of water, which is produced during the esterification.

Also, Zare and coworkers [37] explored the feasibility of some Amberlist catalysts (Amberlyst 15 dry, Amberlyst 16 wet, Amberlite 120-IR), specifically for the esterification of isoamyl alcohol with acetic acid. The Authors compared different activation methods, such as ultrasonic treatment or microwave irradiation, obtaining with the last one the best result (quantitative conversion in 2 h with Amberlist 15 dry).

Bezzekhami and coworkers [46] reported the synthesis of potato starch nanoparticles by Fischer-Speier esterification of starch nanoparticles with rosin acid catalyzed by a proton-exchanged montmorillonite (Maghnite- H^+). Catalyst loading, reaction time, and reaction temperature were optimized by a Design of Experiments approach, and the following reaction parameters were extracted: esterification conducted at 85.7 °C for 23 h, with a catalyst loading of 23.78 wt%.

3. Conclusions and Future Directions

Despite its 130 years, Fisher-Speier esterification is still one of the most employed protocols to obtain esters, and it represents an evergreen topic for academic research. This longevity is related to two main aspects: (I) the importance of esters as intermediates in complex multistep synthesis and fuel industry, and (II) the possibility of improving the outcome of the reaction by developing new and more effective catalysts. Regarding this last aspect, solid acid catalysts, even obtained from waste, represent a field of research that can be further extended soon. It can be expected that there will be an increase in such systems during the next years due to the recent tendency to develop industrial processes modeled on the circular economy. Also, the employment of Lewis acids of the new generation, composed of multiple metals with synergic and cooperative behavior, will be the object of research in the future. In addition, the exploration of basic ionic liquids as catalysts that activate the reaction through hydrogen bonding opened many possibilities for developing new eutectic mixtures able to promote the Fischer-Speier reaction. The possibility to tune the intensity of the hydrogen bond network in eutectic systems by operating on the nature of the hydrogen bond acceptors and donors, as well as on their molar ratio, will result in the development of many systems able to promote the Fischer-Speier esterification. Also, the possibility to play on the hydrophilicity of such systems will soon be exploited to sequester the formed water and thus move the reaction equilibrium toward the products. In the end, what started with a simple and apparently limited mechanism has revealed just

the first step toward chemistry with multiple variables, which can potentially be tuned and customized on the specific synthesis.

Author Contributions: Conceptualization, A.M. (Alberto Mannu) investigation, A.M. (Alberto Mannu); resources, A.M. (Andrea Mele); data curation, A.M. (Alberto Mannu); writing—original draft preparation, A.M. (Alberto Mannu); writing—review and editing, A.M. (Andrea Mele); supervision, A.M. (Alberto Mannu); funding acquisition, A.M. (Andrea Mele). All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No further data are available.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Fischer, E.; Speier, A. Darstellung der Ester. *Chem. Berichte* **1895**, *28*, 3252–3258. [[CrossRef](#)]
2. Steele, J.H.; Bozor, M.X.; Boyce, G.R. Transmutation of Scent: An Evaluation of the Synthesis of Methyl Cinnamate, a Commercial Fragrance, via a Fischer Esterification for the Second-Year Organic Laboratory. *J. Chem. Educ.* **2020**, *97*, 4127–4132. [[CrossRef](#)]
3. Kam, C.M.T.; Levonis, S.M.; Schweiker, S.S. A Visual Organic Chemistry Reaction: The Synthesis of 4-Amino-3-nitrobenzoic Acid Methyl Ester via Fischer Esterification. *J. Chem. Educ.* **2020**, *97*, 1997–2000. [[CrossRef](#)]
4. Salaheldeen, M.; Mariod, A.A.; Aroua, M.K.; Rahman, S.M.A.; Soudagar, M.E.M.; Fattah, I.M.R. Current State and Perspectives on Transesterification of Triglycerides for Biodiesel Production. *Catalysts* **2021**, *11*, 1121. [[CrossRef](#)]
5. Lee, J.-W.; Trinh, C.T. Towards renewable flavors, fragrances, and beyond. *Curr. Opin. Biotechnol.* **2020**, *61*, 168–180. [[CrossRef](#)] [[PubMed](#)]
6. Baij, L.; Hermans, J.; Ormsby, B.; Noble, P.; Iedema, P.; Keune, K. A review of solvent action on oil paint. *Herit. Sci.* **2020**, *8*, 43. [[CrossRef](#)]
7. Godwin, A.D. 26—Plasticizers. In *Plastics Design Library, Applied Plastics Engineering Handbook*, 3rd ed.; Kutz, M., Ed.; William Andrew Publishing: Norwich, NY, USA, 2024; pp. 595–618. ISBN 9780323886673.
8. Mazitova, A.K.; Aminova, G.K.; Vikhareva, I.N. Designing of Green Plasticizers and Assessment of the Effectiveness of Their Use. *Polymers* **2021**, *13*, 1761. [[CrossRef](#)]
9. Karis, D.; Cain, R.; Young, K.; Shand, A.; Holm, T.; Springer, E. Non-fuel uses for fatty acid methyl esters. *Biofuels Bioprod. Biorefining* **2022**, *16*, 1893–1908. [[CrossRef](#)]
10. Campos, J.; Verdeguer, M.; Baur, P. Capped polyethylene glycol esters of fatty acids as novel active principles for weed control. *Pest Manag. Sci.* **2021**, *77*, 4648–4657. [[CrossRef](#)] [[PubMed](#)]
11. Teng, Y.; Lan, P.; White, L.V.; Banwell, M.G. The useful biological properties of sucrose esters: Opportunities for the development of new functional foods. *Crit. Rev. Food Sci. Nutr.* **2023**, *64*, 8018–8035. [[CrossRef](#)] [[PubMed](#)]
12. Nguyen, V.H.; Le, M.N.; Nguyen, H.B.; Ha, K.O.; Pham, T.H.V.; Nguyen, T.H.; Dao, N.S.H.; Nguyen, V.G.; Nguyen, D.L.; Trinh, N.T. Propyl Gallate. *Molbank* **2021**, *2021*, M1201. [[CrossRef](#)]
13. Chaffey, D.R.; Bere, T.; Davies, T.E.; Apperley, D.C.; Taylor, S.H.; Graham, A.E. Conversion of levulinic acid to levulinate ester biofuels by heterogeneous catalysts in the presence of acetals and ketals. *Appl. Catal. B Environ.* **2021**, *293*, 120219. [[CrossRef](#)]
14. Khan, Z.; Javed, F.; Shamair, Z.; Hafeez, A.; Fazal, T.; Aslam, A.; Zimmerman, W.B.; Rehman, F. Current developments in esterification reaction: A review on process and parameters. *J. Ind. Eng. Chem.* **2021**, *103*, 80–101. [[CrossRef](#)]
15. Munawar, S.; Zahoor, A.F.; Hussain, S.M.; Ahmad, S.; Mansha, A.; Parveen, B.; Ali, K.G.; Irfan, A. Steglich esterification: A versatile synthetic approach toward the synthesis of natural products, their analogues/derivatives. *Heliyon* **2024**, *10*, e23416. [[CrossRef](#)]
16. Chen, Y.; Biresaw, G.; Cermak, S.C.; Isbell, T.A.; Ngo, H.L.; Chen, L.; Durham, A.L. Fatty Acid Estolides: A Review. *J. Am. Oil Chem. Soc.* **2020**, *97*, 231–241. [[CrossRef](#)]
17. Altalhi, F.; Algalbati, H.; Magrahi, A. Synthesis of Esters with Different Flavors using Fisher Esterification. *Alq. J. Med. App. Sci.* **2024**, *7*, 884–890. [[CrossRef](#)]
18. Bannon, M.S.; Ellena, J.F.; Gourishankar, A.S.; Marsh, S.R.; Trevisan-Silva, D.; Sherman, N.E.; Jourdan, L.J.; Gourdiec, R.G.; Letteri, R.A. Multi-site esterification: A tunable, reversible strategy to tailor therapeutic peptides for delivery. *Mol. Syst. Des. Eng.* **2024**, *9*, 1215–1227. [[CrossRef](#)]
19. Jayawijayanti, C.A.; Budimarwanti, C. Synthesis of Vanillyl Acetate through Fischer Esterification of Acetic Acid and Vanillyl Alcohol Product of Vanillyl Reduction. *Indones. J. Chem. Environ.* **2022**, *5*, 51–57.
20. Magnani, C.; Fazilati, M.; Kádár, R.; Idström, A.; Evenäs, L.; Raquez, J.-M.; Lo Re, G. Green Topochemical Esterification Effects on the Supramolecular Structure of Chitin Nanocrystals: Implications for Highly Stable Pickering Emulsions. *ACS Appl. Nano Mater.* **2022**, *5*, 4731–4743. [[CrossRef](#)]

21. Villanueva-Solís Luis, A.; Ruíz-Cuilty, K.; Camacho-Dávila, A.; Espinoza-Hicksa, J.C.; González-Sánchez, G.; Ballinas-Casarrubias, L. Lignocellulosic waste pretreatment and esterification using green solvents. *Sep. Purif. Technol.* **2020**, *250*, 117102. [[CrossRef](#)]
22. Song, Y.; Ge, Y.; Zhuo, Y.; Yang, Y.; Liao, Y.-W. Enhancing wettability and water resistance of coatings using tung oleic acid-based gemini wetting agent via Fischer esterification. *Prog. Org. Coat.* **2024**, *197*, 108779. [[CrossRef](#)]
23. Salvitti, C.; de Petris, G.; Troiani, A.; Managò, M.; Di Noi, A.; Ricci, A.; Pepi, F. Sulfuric Acid Catalyzed Esterification of Amino Acids in Thin Film. *J. Am. Soc. Mass Spectrom.* **2023**, *34*, 2748–2754. [[CrossRef](#)] [[PubMed](#)]
24. Ya-Lan, L.; Jin-Yu, P.; Ji-Cong, L.; Wen-Wu, S.; Ji-Kai, L.; Bin, W. Chemo- and Site-Selective Fischer Esterification Catalyzed by B(C₆F₅)₃. *Asian J. Org. Chem.* **2021**, *10*, 1424–1427.
25. Hamerski, F.; Gonçalves Dusi, G.; Trancoso Fernandes dos Santos, J.; Renan da Silva, V.; Pedersen Voll, F.A.; Corazza, M.L. Esterification reaction kinetics of acetic acid and n-pentanol catalyzed by sulfated zirconia. *Int. J. Chem. Kinet.* **2020**, *52*, 499–512. [[CrossRef](#)]
26. Kolet, M.; Atrash, M.; Molina, K.; Zerbib, D.; Albo, Y.; Nakonechny, F.; Nisnevitch, N. Sol–Gel Entrapped Lewis Acids as Catalysts for Biodiesel Production. *Molecules* **2020**, *25*, 5936. [[CrossRef](#)] [[PubMed](#)]
27. Ulfah, M.; Sundari, F.E.; Praputri, E. A Comparison of Palm Fatty Acid Distillate (PFAD) Esterification using Sulphated Alumina versus Sulphuric Acid Catalyst. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *990*, 012015. [[CrossRef](#)]
28. Ranno, L.; Tan, Y.Z.; Ong, C.S.; Guo, X.; Koo, K.N.; Li, X.; Wang, W.; Serna, S.; Liu, C.; Rusli; et al. Crown ether decorated silicon photonics for safeguarding against lead poisoning. *Nat. Commun.* **2024**, *15*, 3820. [[CrossRef](#)]
29. Städtke, K.; Göpfert, A.W.; Inayat, A. Towards a greener synthesis of dianhydrohexitol esters. *Green Chem.* **2023**, *25*, 7292. [[CrossRef](#)]
30. Jansen, J.H.; Powell, A.B.; Specht, S.E.; Gerislioglu, S.; Hermans, I. Understanding the Structure and Reactivity of Mixed Titanium(IV) Alkoxide and Tin(II)/(IV) Carboxylates as Esterification Catalysts. *ACS Sustain. Chem. Eng.* **2022**, *10*, 2484–2493. [[CrossRef](#)]
31. De Bruyne, A.; Stuyck, W.; Deleu, W.; Leinders, J.; Marquez, C.; Janssens, K.; Sakellariou, D.; Ghillebert, R.; De Vos, D.E. Efficient two-step production of biobased plasticizers: Dehydration-hydrogenation of citric acid followed by Fischer esterification. *Green Chem.* **2023**, *25*, 3896. [[CrossRef](#)]
32. Zaharani, L.; Khaligh, N.G.; Johana, M.R.; Gorjian, H. Synthesis and characterization of a new acid molten salt and the study of its thermal behavior and catalytic activity in Fischer esterification. *New J. Chem.* **2021**, *45*, 7081. [[CrossRef](#)]
33. da Luz Correa, A.P.; Cardoso Bastos, R.R.; da Rocha Filho, G.N.; Zamian, J.R.; Vieira da Conceição, L.R. Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction. *RSC Adv.* **2020**, *10*, 20245. [[CrossRef](#)]
34. Lawer-Yolar, G.; Dawson-Andoh, B.; Atta-Obeng, E. Synthesis of Biodiesel from Tall Oil Fatty Acids by Homogeneous and Heterogeneous Catalysis. *Sustain. Chem.* **2021**, *2*, 206–221. [[CrossRef](#)]
35. Fawaz, E.G.; Salam, D.A.; Daou, T.J. Esterification of linoleic acid using HZSM-5 zeolites with different Si/Al ratios. *Microporous Mesoporous Mater.* **2020**, *294*, 109855. [[CrossRef](#)]
36. Russo, V.; Taddeo, F.; Cogliano, T.; Vitiello, R.; Esposito, R.; Tesser, R.; Salmi, T.; Di Serio, M. Investigation of the intrinsic reaction kinetics and the mass transfer phenomena of nonanoic acid esterification with 2-ethylhexanol promoted by sulfuric acid or Amberlite IR120. *Chem. Eng. J.* **2021**, *408*, 127236. [[CrossRef](#)]
37. Zare, M.; Golmakani, M.-T.; Sardarian, A. Green synthesis of banana flavor using different catalysts: A comparative study of different methods. *Green Chem. Lett. Rev.* **2020**, *13*, 83–92. [[CrossRef](#)]
38. Bano, K.; Jain, A.; Sarkar, R.; Panda, T.K. Economically Viable and Efficient Catalysts for Esterification and Cross Aldol Condensation Reactions under Mild Conditions. *ChemistrySelect* **2020**, *5*, 4470–4477. [[CrossRef](#)]
39. Hussein, M.F.; El Naga, A.O.A.; El Saied, M.; AbuBaker, M.M.; Shaban, S.A.; El Kady, F.Y. Potato peel waste-derived carbon-based solid acid for the esterification of oleic acid to biodiesel. *Environ. Technol. Innov.* **2021**, *21*, 101355. [[CrossRef](#)]
40. Xiao, K.; Zhou, Z.; Ye, C.; Chen, J.; Qiu, T. Hydrogen bond induced acidic solids for effective esterification catalysis. *Chem. Eng. J.* **2023**, *478*, 147398. [[CrossRef](#)]
41. Zhu, J.; Jiang, W.; Yuan, Z.; Lu, J.; Ding, J. Esterification of tall oil fatty acid catalyzed by Zr⁴⁺-CER in fixed bed membrane reactor. *Renew. Energy* **2024**, *221*, 119760. [[CrossRef](#)]
42. Zhang, B.; Gao, M.; Geng, J.; Cheng, Y.; Wang, X.; Wu, C.; Wang, Q.; Liu, S.; Cheung, S.M. Catalytic performance and deactivation mechanism of a one-step sulfonated carbon-based solid-acid catalyst in an esterification reaction. *Renew. Energy* **2021**, *164*, 824–832. [[CrossRef](#)]
43. Masteri-Farahani, M.; Hosseini, M.-S.; Forouzeshfar, N. Propyl-SO₃H functionalized graphene oxide as multipurpose solid acid catalyst for biodiesel synthesis and acid-catalyzed esterification and acetalization reactions. *Renew. Energy* **2020**, *151*, 1092e1101. [[CrossRef](#)]
44. Chandrika, B.; Muraleedharan, S.; Chandran, G. Kinetics and mechanism of esterification of palmitic acid with ethanol in the presence of Brønsted acidic ionic liquids as catalyst. *Oxf. Open Mater. Sci.* **2024**, *4*, itae006. [[CrossRef](#)]
45. Hong, S.-M.; Kim, O.Y.; Hwang, S.-H. Synthesis of 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene di (mercaptopropionate) for high-luminance and refractive prism sheets. *Prog. Org. Coat.* **2024**, *196*, 108700. [[CrossRef](#)]

46. Bezzekhami, M.A.; Harrane, A.; Belalia, M.; Mostefai, A.; Belkhir, N.L.; Bououdina, M. Green Synthesis of Starch Nanoparticles (SNPs) by Esterification with Rosin Acid Catalyzed by Maghnite-H⁺ (Algerian Montmorillonite) with Enhanced Antioxidant Activity. *Arab. J. Sci. Eng.* **2023**, *48*, 311–326. [[CrossRef](#)]
47. Zaharani, L.; Ghafarikhaligh, M.; Rafie, M.J.; Khaligh, M.G. Single crystal XRD and FTIR studies of 4H,4H'-trimetylenedipiperidine-dium hydrogen sulfate hydrate and investigation its catalytic activity in Fischer esterification using the in-situ continuous liquid–liquid extraction technique. *Res. Chem. Intermed.* **2023**, *49*, 5451–5469. [[CrossRef](#)]
48. Wolzak, L.A.; van der Vlugt, J.I.; van den Berg, K.J.; Reek, J.N.H.; Tromp, M.; Korstanje, T.J. Titanium-catalyzed esterification reactions: Beyond Lewis acidity. *ChemCatChem* **2020**, *12*, 5229–5235. [[CrossRef](#)]
49. Melchiorre, M.; Cucciolito, M.E.; Di Serio, M.; Ruffo, F.; Tarallo, O.; Trifuoggi, M.; Esposito, R. Homogeneous Catalysis and Heterogeneous Recycling: A Simple Zn(II) Catalyst for Green Fatty Acid Esterification. *ACS Sustain. Chem. Eng.* **2021**, *9*, 6001–6011. [[CrossRef](#)]
50. Wu, S.; Wang, Y.; Tao, H.; Yu, Z.; Wu, L.; Meng, X.; Zhang, Y. Fischer Esterification of Benzoic Acid and Polyhydric Alcohols Catalyzed by Basic Ionic Liquids of Bisimidazolium Tungstates. *ChemistrySelect* **2023**, *8*, e202204112. [[CrossRef](#)]
51. Alsalam, M.; Chermahini, A.N.; Dinari, M.; Luque, R.; Pineda, A.; Vargas Fernandez, C. Synthesis of carrageenan/DFNS composite and its application in the esterification of levulinic acid with alcohols. *Inorg. Chem. Commun.* **2024**, *169*, 113054. [[CrossRef](#)]
52. Chung, S.-H.; Demetriou, M.; Wang, H.; Shiju, N.R. Solid acid catalyzed esterification of dicyclopentadiene with organic acids to bio-based functional monomers. *Sustain. Energy Fuels* **2024**, *8*, 1788–1792. [[CrossRef](#)]
53. Teasdale, A.; Delaney, E.J.; Eyley, S.C.; Jacq, K.; Taylor-Worth, K.; Lipczynski, A.; Hoffmann, W.; Reif, V.; Elder, D.P.; Facchine, K.L.; et al. A Detailed Study of Sulfonate Ester Formation and Solvolysis Reaction Rates and Application toward Establishing Sulfonate Ester Control in Pharmaceutical Manufacturing Processes. *Org. Process Res. Dev.* **2010**, *14*, 999–1007. [[CrossRef](#)]
54. Van Loon, L.L.; Allen, H.C. Methanol Reaction with Sulfuric Acid: A Vibrational Spectroscopic Study. *J. Phys. Chem. B* **2004**, *108*, 17666–17674. [[CrossRef](#)]
55. Wu, S.; Huang, J.; Wang, Y.; Tao, H.; Yu, Z.; Zhang, Y. Bisimidazolium Tungstate Ionic Liquids: Highly Efficient Catalysts for the Synthesis of Linear Organic Carbonates by the Reaction of Ethylene Carbonate with Alcohols. *Catal. Lett.* **2023**, *153*, 62–73. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.