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Unconventional media and technologies for starch etherification and esterification

Alexandre Gilet^{a,c}, Claude Quettier^b, Vincent Wiatz^b, Hervé Bricout^a, Michel Ferreira^a, Cyril Rousseau^a, Eric Monflier^a, Sébastien Tilloy^{*a}

Among the most widespread starch derivatives, etherified and esterified starches play an important role. These derivatives are generally prepared by using thermal energy and conventional solvents. This review summarizes the recent advancements in etherification and esterification of starch in unconventional media, i.e. ionic liquids or supercritical CO₂, and by employing unconventional technologies, i.e. microwaves, ultrasounds or ball-milling. The present contribution aims to provide an overview to help researchers seeking an alternative medium or technology to functionalize starch. The green aspects of unconventional approaches were presented and physical-chemical properties of modified starches obtained by these approaches were also described. Whenever possible, the advantages and disadvantages of each system are discussed. Finally, even if it is not always mentioned in the publications, the use of these experimental conditions probably lead to a partial degradation of starch molecular structure.

1. Introduction

Starch is the main energy storage in plants and one of the most abundant polysaccharide, being second behind cellulose. It is extracted from various sources, the major ones being tubers (potato, cassava) and cereals (wheat, corn, rice) as white granules that differ in size and shape according to the source. Those granules are mainly composed of two D-glucose homopolymers that are amylose and amylopectin. These two molecules mainly differ by their structure as amylose is linear with glucose units bound together with α -1,4 bonds while amylopectin shows a grape-like structure as 5% of the glucose units are branched with α -1,6 bonds.^{1 2 3} Starch is largely employed as a resource for industry because of its low-price, renewability and biodegradability. However, the use of starch is limited by several drawbacks such as insolubility in cold water and its strong tendency for the gels towards retrogradation and syneresis. To circumvent these disadvantages and to find extended applications, modifications of this natural polymer can be realised (Fig. 1).^{4 5} The obtained starch derivatives found a wide variety of application like (i) in building materials to reduce the setting time,^{6 7} (ii) in drilling fluid to increase its viscosity⁸ (iii) in water treatment because of their flocculating properties and as a substitute to polyacrylamide,^{9 10} (iv) in the composition of detergents as a redeposition inhibitor of dirt,¹¹ (v) into plastics to make them more biodegradable or oxo-biodegradable,¹² (vi) in formulation in the pharmaceutical industry,¹³ and (vii) as a sizing agent and wet strength additive for paper.^{14 15}

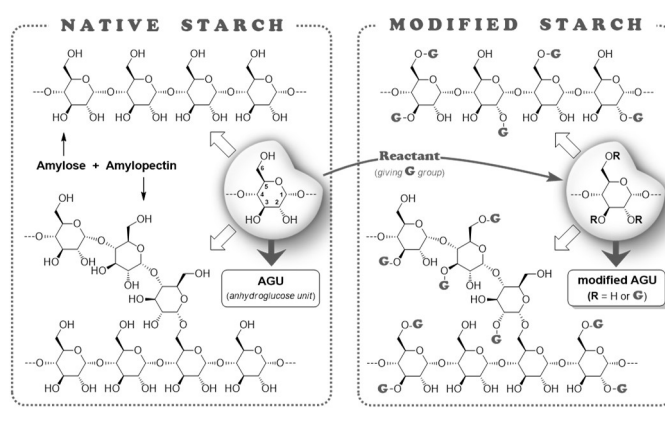


Fig. 1. General structures of native and modified starch

These starch derivatives are generally synthesized by classical technologies (thermal energy) and in conventional solvents. Interestingly, there is a growing interest in the scientific literature for the association of starch and unconventional media (ionic liquids, supercritical CO₂) or unconventional technologies (microwaves, ultrasounds, ball-milling). Indeed, since the last 30 years, the number of Web of Science®-indexed publications related to the topics starch/ionic liquids, starch/supercritical CO₂, starch/microwaves, starch/ultrasounds or starch/ball-milling was increased (Fig. 2).

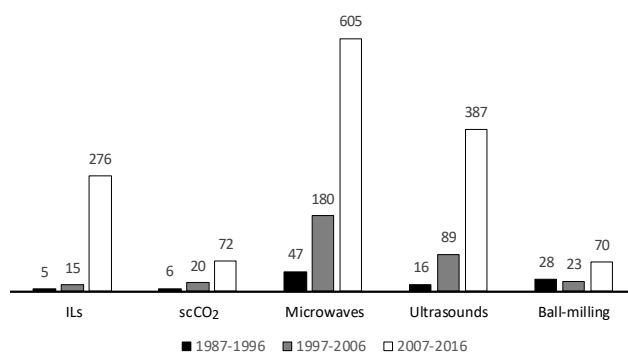


Fig. 2. Number of publications given by Web of Science® during the period 1987-2016 by using starch/ionic liquids (ILs), starch/supercritical CO₂ (scCO₂), starch/microwaves, starch/ultrasounds and starch/ball-milling as topics.

Among the most widespread starch derivatives, esterified and etherified starches play an important role. Esterified starches are generally synthesized by classical technologies (thermal energy) and in conventional solvents such as pyridine,^{16 17 18} dioxane and toluene,¹⁹ DMAc/LiCl,²⁰ or DMSO.²¹ Etherification of starch with fatty epoxides or alkyl chlorides can be performed in water^{22 23} or in DMSO.^{24 25 26} Typically, the most widespread industrial functionalization processes are performed in aqueous dispersion, enabling conversion up to degrees of substitution of 0.3-0.4 by retaining the granular structure of starch. These processes can reach higher DS by handling a viscosity constraint connected to granule disruption.²⁷ Numerous articles or reviews concerning esterified and etherified starches have been published.^{28 29 5 30 31 32 33 34} Nevertheless, the chemical modifications of starch in unconventional media and by unconventional technologies have not been notably reviewed previously in a single publication. In this context, the aim of this review is to summarize the recent advances in etherification and esterification of starch in ionic liquids, in supercritical CO₂ and by using microwaves, ultrasounds or ball-milling over the period 2010-2016. In each case, the experimental conditions used to obtain the highest degree of substitution (DS) were selected in order to highlight the efficiency of each system. This review could help researchers seeking an alternative medium or technology to functionalize starch. Whenever possible, the advantages and disadvantages of each system are discussed.

2. Unconventional media for chemical modifications of starch

2.1 Chemical modifications of starch in ionic liquids

Over the last few years, the application of ionic liquids (ILs) in polysaccharide chemistry has received major attention.³⁴ Because of their unique properties such as low melting point, low vapor pressure, non-flammability, and recyclability, they have been considered as possible green substitutes for toxic organic solvents. Among them, 1-*N*-butyl-3-methylimidazolium chloride (BMIM⁺,Cl⁻) is the most widespread ionic liquid used to solubilize/modify native starch. Indeed, starch can be dissolved in this solvent up to 15% weight at 80°C.³⁴ Chemical modifications of native starch in ILs mostly included etherification and esterification (Table 1).

Literature concerning starch etherification in ionic liquids is very limited. Xie et al. described in 2010 the synthesis of a cationic corn starch by reacting the native starch with glycidyltrimethylammonium chloride (GTAC) in BMIM⁺,Cl⁻ (Table 1, entry 1).³⁵ The reaction was catalysed by sodium hydroxide and optimisation of the reaction conditions (80°C, reaction time 2h, AGU:GTAC:catalyst molar ratio of 1:3:0.135) led to a maximum substitution degree of 0.99. A strong influence of the catalyst was observed as a small quantity was needed for the reaction to occur efficiently while increasing the base amount led to a reduction of the DS explained by the GTAC hydrolysis. In this study, recycling experiments of the ionic liquid

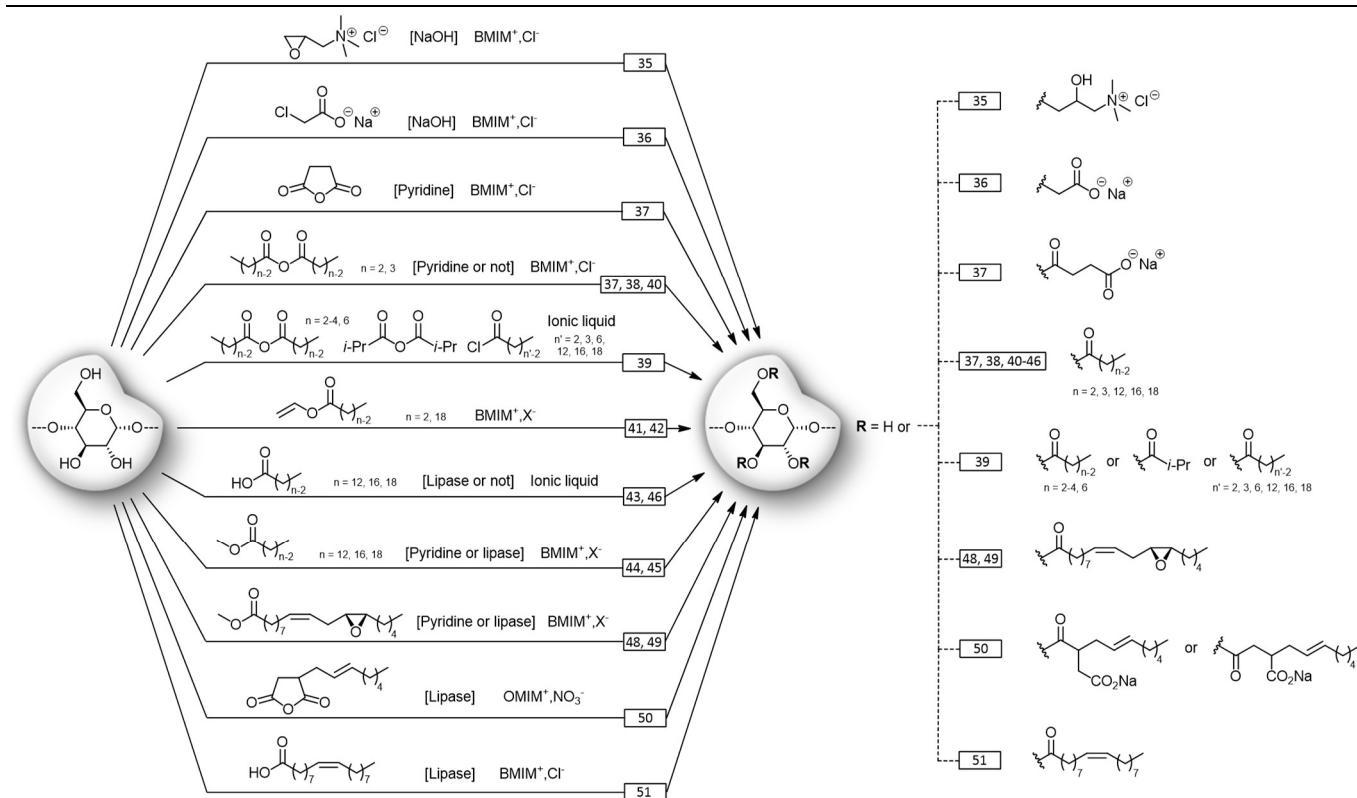
were done and showed that the reaction medium could be reused up to four times without significant decrease in the DS. Differential scanning calorimetry (DSC), ¹H nuclear magnetic resonance (NMR), X-ray diffraction (XRD) patterns, scanning electron micrographs (SEM) images and thermal gravimetric analysis (TGA) measurements were used to characterize the synthesized starches. The authors concluded that a homogeneous modification of native starch was observed as the starch granules lost their crystalline structure when dissolved in the ionic liquid. Indeed, hydroxyl groups became more accessible to the reactant, which was reflected in an efficient and uniform modification.

The same group described the synthesis of an anionic corn starch using also BMIM⁺,Cl⁻ as the reaction medium (Table 1, entry 2).³⁶ The reaction between starch and sodium monochloroacetate (SMCA) was studied by varying reagent and catalyst amounts as well as reaction time and temperature. The optimum conditions led to a DS value of 0.76 within 3h at 90°C with ratio of NaOH and SMCA to AGU of 1.2 and 1 respectively. Once again, the recyclability of the ionic liquid was investigated. Although some by-products are told to be formed during the reaction, similar DS values (0.75 – 0.66) are reached after five recycling experiments. Again, the previously cited analytical techniques were used to characterize the modified starches. The same conclusions can be drawn as a homogeneous substitution was obtained due to the destruction of the ordered native starch crystalline structure.

Publications dealing with starch esterification in ionic liquids are more common and the products range from starch acetates to starch fatty esters. In 2010, Xie et al. described the pyridine-catalyzed acetylation of corn starch with acetic anhydride in BMIM⁺,Cl⁻ (Table 1, entry 3).³⁷ At an optimal reaction temperature of 100°C, starch acetates with a low DS (< 0.18) were obtained without catalyst at different reaction time and reactant ratio. By adding 3 equivalents of pyridine by AGU, and after 3h of reaction, a starch acetate with the highest DS of 2.35 was obtained. This DS value was reached for a reactant/AGU molar ratio of 5:1. Similar optimum reaction conditions were observed with succinic anhydride as reactant, although a longer time was needed (4h) to reach a DS value of 0.93. The lowest value obtained in this case was told to be due to the lowest reactivity of the succinic anhydride compared to the acetic anhydride because of its steric hindrance. Starch esters characterizations via SEM and XRD analysis showed a conversion of the crystalline structure into amorphous state in the ionic liquid. Recycling of the solvent was also considered. A decrease in the DS was observed after the recycling experiments but was not significant for up to 5 cycles.

Later, Luo et al. obtained similar results in the acetylation of corn starch without catalyst (Table 1, entry 4).³⁸ The key step was the starch dissolution in BMIM⁺,Cl⁻ at 105°C for 2h before reaction. The complete dissolution of starch after 2h was simultaneously proved by polarized micrographs and XRD patterns of starch which showed no more crystallinity. Maximum DS of 2.11 was obtained within 2h of reaction at 105°C with an acetic anhydride / AGU ratio of 5:1. XRD

Table 1 Chemical modifications of starch in ionic liquids (surrounded numbers in the scheme correspond to bibliographic references, column Ref. in the table)



Entry	Substrate	Reactant	Reactant / AGU ^a	Product	Solvent	Experimental conditions	Catalyst (Cata./AGU ^a)	DS	Ref.
1	Corn starch	Glycidyltrimethyl ammonium chloride	0.5-4	Starch ether	BMIM ⁺ ,Cl ⁻	70-110°C 1-8h	NaOH (0.135-3)	0.021-0.99	35
2	Corn starch	Sodium mono-chloroacetate	0.4-1.6	Starch ether	BMIM ⁺ ,Cl ⁻	70-110°C 1-5h	NaOH (0.4-2)	0.31-0.76	36
3	Corn starch	Acetic or succinic anhydride	1-6	Starch esters	BMIM ⁺ ,Cl ⁻	70-110°C 1-5h	Pyridine (1-3)	0.04-2.35 (AA) 0.02-0.93 (SA)	37
4	Corn starch	Acetic anhydride	2-6	Starch acetate	BMIM ⁺ ,Cl ⁻	75-115°C 0.5-2.5h	-	0.1-2.11	38
5	Corn starch	Acid anhydrides / Acyl chlorides	2.25, 4.5 / 0.5	Starch mixed esters	Reactant	95-115°C 1.5h	IL (0.3-0.7)	0.79-3 (ΣDS)	39
6	Maize starch	Acetic or propionic anhydride	1.5-4.5	Starch esters	Reactant	110-150°C 1-4h	IL, mainly BMIM ⁺ ,Cl ⁻ (0.0188-1.2)	0.05-2.89 (AA) 0.77-2.86 (PA)	40
7	Corn maltodextrin	Vinyl acetate	1 or 3	Starch acetate	BMIM ⁺ ,X ⁻	40°C 70h	-	0.008-1.8	41
8	Maltodextrin	Vinyl stearate	0.1-3	Maltodextrin stearate	BMIM ⁺ ,dca ⁻	75°C 69h	-	0.069-2.4	42
9	Corn starch	Lauric, palmitic or stearic acid	1	Starch esters	IL or DMSO or DMF	100-140°C 3h	-	0.023-0.105 (L) 0.032-0.098 (P) 0.038-0.092 (S)	43
10	Corn starch	Methyl laurate or stearate	1-4	Starch esters	BMIM ⁺ ,Cl ⁻	100-140°C 1-6h	Pyridine (0-3)	0.15-0.37 (ML) 0.12-0.28 (MS)	44
11	High-amylose maize starch	Methyl palmitate	1-4	Starch palmitate	BMIM ⁺ ,BF ₄ ⁻ / BMIM ⁺ ,OAc ⁻ mixtures	50-80°C 1-4h	<i>Candida rugosa</i> lipase	0.034-0.153	45
12	High-amylose maize starch	Lauric acid	1-4	Starch laurate	BMIM ⁺ ,BF ₄ ⁻	50-80°C 3-11h	<i>Candida rugosa</i> lipase	0.048-0.171	46
13	Cassava starch	Vernolic acid methyl ester	3	Starch vernolate	BMIM ⁺ ,PF ₆ ⁻ / DMSO (3/1 vol.)	40°C 72h	Novozyme 435	0.95	48

14	Cassava starch	Vernolic acid methyl ester	3	Starch vernolate	BMIM ⁺ ,Cl ⁻	110°C 24h	Pyridine (6)	1.03	49
15	Waxy maize starch	Octenyl succinic anhydride	0.023	Esterified starch	C ₈ MIM ⁺ ,NO ₃ ⁻	40-70°C 1-7h	Novozyme 435 lipase	0.0006-0.013	50
16	Potato starch	Oleic acid	3	Starch oleate	BMIM ⁺ ,Cl ⁻	60-80°C 4-8h	<i>Thermomyces lanuginosus</i> lipase	0.09-0.22	51

^a molar ratio.

patterns of the synthesized acetylated starches showed the appearance of new diffraction peaks due to the formation of new structures. Thermal stability of the new products was studied by TGA and showed a beneficial effect of the acetylation towards thermal stability. Alternatively, ionic liquids can be used, instead of pyridine, as esterification catalyst. Indeed, in 2010, Volkert *et al.* described the synthesis of corn starch mixed esters (mainly starch acetate laurates) catalysed by an ionic liquid in the form of imidazolium salts generated *in situ* during the reaction (Table 1, entry 5).³⁹ Three different corn starch sources with varied amylose content were used in this study. The starch was firstly suspended/reacted in the corresponding anhydride (acetate or propionate) for 45 min at 95°C. An imidazole derivative with a carboxylic acid chloride were then added to the mixture heated at 115°C during 45 min with an extra acid anhydride amount. As an acid scavenger, the imidazole derivative spontaneously formed the imidazolium chloride salt which catalysed the starch esterification. Different imidazole components were tested and in almost all cases the total DS exceeded 2. The highest DS of 0.14 in laurate moiety was obtained with 1-acetylimidazole, whereas acetate DS in the mixed ester starch was 2.63. By following this strategy, trifunctional starch mixed esters could be synthesized by simply replacing the second extra amount of acid anhydride by a different one. Mechanical properties of the new starches were very good and the humidity uptake in the samples, which was known to be a disadvantage, was reduced to 0.5% wt instead of 12-14% for the native starches. The same team subsequently described the reaction of high amylose maize starch in acetic or propionic anhydride as solvent and catalysed by ILs (Table 1, entry 6).⁴⁰ In this work, studies on starch degradation received a special attention. One reason why high DS was obtained within 4h at 130°C (DS = 2.7 with a Ac₂O / AGU ratio of 4.5 and a BMIM⁺,Cl⁻ / AGU ratio of 0.2) was the activation effect of the IL on the acetic acid formed as by-product. In all cases, a starch degradation more or less pronounced was observed due to the acidic nature of the ILs used. This degradation is favoured at high temperatures (150°C). Different ILs with varying chain length (1-*N*-methylimidazolium chloride HMIM⁺,Cl⁻, 1-*N*-ethyl-3-methylimidazolium chloride EMIM⁺,Cl⁻, 1-*N*-butyl-3-methylimidazolium chloride and 1-*N*-hexyl-3-methylimidazolium chloride) were tested and a DS decrease was observed when the chain length was increased. This phenomenon was attributed to a reduction in the effective chloride ion concentration which led to a lower partial starch solubilisation. Furthermore, the highest esterification rate along with the highest starch degradation were obtained with the solvent HMIM⁺,Cl⁻ due to its additional acidic character. Different counterions were also tested, and halides gave higher DS compared to other ions. Finally, the authors showed that the addition of pyridine in the reaction mixture could lead to a decrease in the starch degradation. Furthermore, the average molar mass of the starch acetate synthesised could be tuned by the amount of pyridine used.

In 2010, Shogren *et al.* conducted the acetylation of corn maltodextrin without catalyst at 40°C during 70h by transesterification with vinylacetate in different BMIM⁺,anion⁻ ionic liquids as solvent (Table 1, entry 7).⁴¹ The DS obtained was in the

range 0.008 – 1.8 depending on the counteranion used. Basic anions such as dicyanamide (dca) or acetate gave the highest DS (1.10 and 1.8 respectively) while neutral anions gave low DS (0.12 and 0.008 for NO₃⁻ and Cl⁻ respectively). Specific selectivity in C₂ position occurred when acetylation was performed in BMIM⁺,dca⁻ while uniform acetylation was observed in BMIM⁺,OAc⁻. No significant changes in the product molecular weight were detected proving that no particular starch degradation occurred.

Another paper of the same group described the synthesis of maltodextrin stearates, via a similar strategy (75°C / 69h), with vinylstearate as reactant and BMIM⁺,dca⁻ as solvent (Table 1, entry 8).⁴² DS ranged from 0.069 to 2.4 depending on the reactant quantity (molar ratio reactant / AGU of 0.1 or 3 respectively). Again, when BMIM⁺,OAc⁻ was used instead of BMIM⁺,dca⁻, lower DS was obtained. The new products showed interesting physical properties such as very hydrophobic surface or optical birefringence suggesting liquid crystal formation.

Another team described the synthesis of fatty-acid starch esters without catalyst starting from corn starch and lauric (CH₃(CH₂)₁₀COOH), palmitic (CH₃(CH₂)₁₄COOH) or stearic acid (CH₃(CH₂)₁₆COOH) in different ILs, organic solvents or mixtures thereof (Table 1, entry 9).⁴³ For all solvents used, the DS of the product decreased when the reactant alkyl chain length increased. Under the experimental conditions used, the obtained DS followed the order DMSO > BMIM⁺,Cl⁻/DMSO > EMIM⁺,OAc⁻ > BMIM⁺,Cl⁻ > DMF. Optimum temperature was found to be 120°C. Higher temperatures resulted in starch degradation. Among the different ILs used, a maximum DS of 0.1 for starch laurate was obtained after 3h at 120°C in BMIM⁺,Cl⁻ / DMSO mixture (ratio 3:1) with a lauric acid / AGU molar ratio of 1:5.

Two of these previous acids were also used in their methyl ester form by Xie *et al.* Indeed, they investigated the reaction between corn starch and methyl laurate or methyl stearate in the presence of pyridine in BMIM⁺,Cl⁻ (Table 1, entry 10).⁴⁴ By varying different parameters such as catalyst nature, catalyst amount, temperature, reaction time and fatty acid methyl ester / AGU ratio, they optimised the reaction conditions and obtained a maximum DS of 0.37 for starch laurate at 120°C in 2h with fatty ester / pyridine / AGU molar ratio of 4:1:1 and a maximum DS of 0.28 for starch stearate at 110°C in 2h with fatty ester / pyridine / AGU molar ratio of 4:2:1. SEM and XRD techniques were used to characterize the resulting starch esters and showed that starch granules were destroyed and the crystalline structure was lost after modification. Recycling experiments of the IL phase were realized and did not show any significant decrease in the DS after 4 runs.

More recently, starch esterification was also conducted in ILs using biocatalysts. Indeed, in 2012, starch palmitates were synthesised in BMIM⁺,BF₄⁻ / BMIM⁺,OAc⁻ mixtures in the presence of the *Candida rugosa* lipase (Table 1, entry 11).⁴⁵ The mixture composition of the IL should be chosen with care. Indeed, BMIM⁺,OAc⁻ is able to solubilise the high amylose maize starch but it also reduces the lipase activity. On the other hand, BMIM⁺,BF₄⁻ cannot dissolve starch but is a benign solvent for biocatalysis reactions. The maximum DS value of 0.144

was obtained for a $\text{BMIM}^+\text{BF}_4^- / \text{BMIM}^+\text{OAc}^-$ mass ratio of 19:5 at 60°C during 3h with a reactant / AGU ratio of 3:1. A slightly higher DS of 0.153 could be reached by increasing the lipase dosage from 0.1g to 0.2g. Therefore, the excess amount of enzyme was suggested to have no sufficient influence on the reaction. SEM and XRD patterns of the modified starches showed a large disruption in morphology/crystallinity and TGA analysis suggested a decrease in thermal stability. However, water contact angle measurements indicated an increased hydrophobicity.

Later, the same group described the enzymatic synthesis of starch laurates in $\text{BMIM}^+\text{BF}_4^-$ starting from high amylose maize starch and lauric acid (Table 1, entry 12).⁴⁶ In this publication, the authors used a two-step method which consisted in firstly doing the pregelatinization of the starch in BMIM^+Cl^- in order to destroy its granular structure and secondly adding the dried pregelatinized starch to $\text{BMIM}^+\text{BF}_4^-$ for the lipase esterification. Among the different lipases screened, *Candida rugosa* achieved the highest DS value of 0.165 at 60°C for 5h with a lipase dosage of 0.3g and a reactant / AGU molar ratio of 3:1. The heterogeneous nature of the system composed of the pregelatinized starch in $\text{BMIM}^+\text{BF}_4^-$ was told to be responsible for the extension of the reaction time (5h) compared to what was observed in their previous study relating to the enzymatic starch esterification in $\text{BMIM}^+\text{BF}_4^-/\text{BMIM}^+\text{OAc}^-$ homogeneous systems (3h). The efficiency of the above described procedure in ILs was supported by the maximum DS value of only 0.018 obtained in prior studies realised on enzymatic starch esterification with fatty acids in water.⁴⁷ Characterization of the modified starches via SEM, XRD and TGA resulted in the same observations than their previous study concerning starch palmitates.

Another group used vernonia oil, consisting of vernolic acid methyl ester (epoxy ester), to esterify cassava starch. In a first set of experiments, enzymatic reaction was performed in a mixture of $\text{BMIM}^+\text{PF}_6^-$ and DMSO (20 wt%) using the lipase *Candida Antarctica* fraction B (Novozyme 435) (Table 1, entry 13).⁴⁸ This solvent was selected to be a good compromise between starch solubility and lipase activity. Starch vernolate with DS of 0.95 was obtained after 72h at 40°C and with a reactant / AGU molar ratio of 3:1. The DS close to 1 was suggested to be the consequence of a high selectivity towards one hydroxyl group of the AGU. FTIR and solid state NMR analysis confirmed that both epoxide and alkene functionalities, coming from the vernolic ester, were retained in the synthesised starch, offering the possibility of further modifications. SEM and XRD studies showed a modification of morphology and crystallinity of native starch producing an amorphous material. Thermal behaviour was also affected with a strong decrease in transition temperatures of the starch vernolate compared to native cassava starch.

Later, the same group described a method using pyridine as catalyst (Table 1, entry 14).⁴⁹ In this new method the solvent was replaced by BMIM^+Cl^- , reaction temperature and time were respectively increased to 110°C and 24h. Again, the functionalities of methyl vernolate were still present in the synthesised starch with a DS value of 1.03.

Although the DS between these 2 methods were comparable (0.95 for the enzymatic reaction and 1.03 for the pyridine catalysed reaction), difference in melting points was spotted (87.9°C and 111.4°C respectively for enzymatic and pyridine catalysed reaction). The authors suggested a difference in selectivity between the two methods as enzyme catalysed reaction would have led to a more pronounced functionalisation of the AGU C6 carbon whereas pyridine catalysed reaction would not be selective.

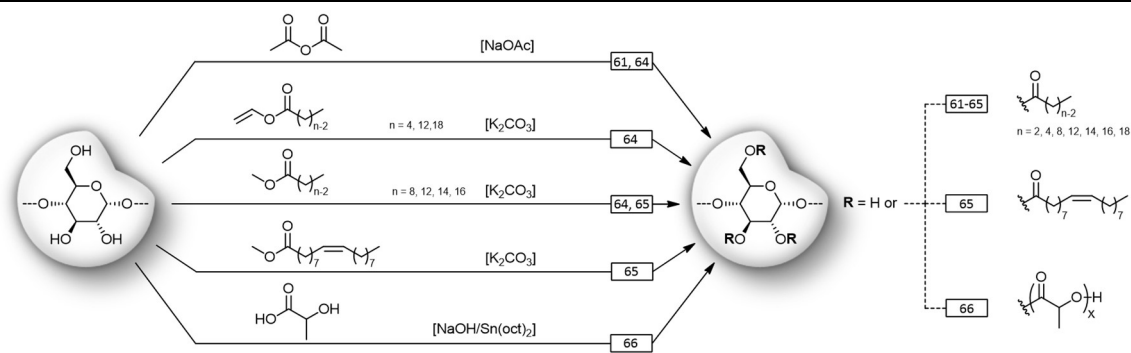
Most recently, octenyl succinic anhydride (OSA) was used as reactant to enzymatically modify waxy maize starch in 1-octyl-3-methylimidazolium nitrate ($\text{OMIM}^+\text{NO}_3^-$) (Table 1, entry 15).⁵⁰ Native starch underwent a pregelatinization step in BMIM^+Cl^- before being reacted with OSA in $\text{OMIM}^+\text{NO}_3^-$, and in the presence of Novozyme 435 lipase as catalyst. Different experimental conditions were applied by varying starch concentration, lipase dosage, reaction temperature and reaction time. A DS value of 0.013 was reached for the subsequent optimized conditions: starch concentration 5wt%, lipase dosage 1wt%, reaction temperature of 50°C, reaction time of 3h. Slightly higher DS could be obtained by increasing the lipase dosage from 1wt% to 2wt%. However, this DS increase was not high enough to work at this dosage. The temperature increase from 50°C to 70°C led to a DS decrease caused by lipase inactivation and longer reaction time led to enhancement of the hydrolytic lipase activity due to the water formation during reaction. SEM and XRD analysis suggested that gelatinization/dissolution of native starch in the IL was the main reason for the destruction of the structure/crystallinity of native starch. Again, thermal analysis showed a decrease in the initial temperature of degradation which was already ascribed to the disruption of granular structure during dissolution/modification process.

Lately, potato starch was biocatalytically esterified with oleic acid in BMIM^+Cl^- (Table 1, entry 16).⁵¹ The enzyme used was an immobilised fungal lipase from *Thermomyces Lanuginosus*. The reactant was chosen for its potential further modifications on the unsaturated double bond. The main advantage of the described method is the easiest work-up since only one ionic liquid is both used for pregelatinisation and reaction. The highest DS of 0.22 was obtained for the reaction realized at 60°C for 4h. Higher temperature and longer reaction time led to a decrease in the DS due to the formation of water as by-product that could favour hydrolytic reactions. Thermal stability of starch oleates was decreased showing a reduction of the initial decomposition temperature.

2.2 Chemical modifications of starch in densified CO₂

Possessing the advantages of being a non-flammable and a non-toxic solvent, inert toward a lot of chemical species and easy to remove after reaction by simple depressurization, densified CO₂ was used with success as reaction medium for chemical modification of starch.⁵² This success probably comes from the fact that, in addition to a pressure effect,^{53 54} densified CO₂, and in particular supercritical CO₂ (*i.e.* CO₂ whose temperature and pressure are respectively above 31 °C and 74 bar) is able to change the properties of starch. In particular, a treatment of starch by supercritical CO₂ (scCO₂) tends to

Table 2 Chemical modifications of starch in densified carbon dioxide (surrounded numbers in the scheme correspond to bibliographic references, column Ref. in the table)



Entry	Substrate ^a	Reactant	Reactant / AGU ^b	Product	Solvent	Experimental conditions	Catalyst (Cata./AGU ^b)	DS ^c	Ref.
1	Potato starch (15.2 wt% H ₂ O)	Acetic anhydride	2-5	Starch acetate	CO ₂	40-90°C; 1h; 60-98 bar	NaOAc (0-0.8)	0.03-0.46	61
2	Potato starch (15.2 wt% H ₂ O)	Acetic anhydride	4.35	Starch acetate	CO ₂	50-90°C; 1-24h; 80-250 bar	K ₂ CO ₃ mainly (0.1-0.5)	0.04-0.96	62
3	Potato starch (16.2 wt% H ₂ O)	Acetic anhydride	4.35	Starch acetate	CO ₂	90°C; 1-24h; 80-250 bar	NaOAc (0.1)	0.22-0.62	63
4	Potato starch (16.2 wt% H ₂ O)	Vinyl/Methyl esters and anhydrides (C4-C18)	3	Starch esters	CO ₂	120-150°C; 6-18h; 60-250 bar	K ₂ CO ₃ (0.1)	0.003-0.31	64
5	Sago starch (16.9 wt% H ₂ O)	Methyl esters (C12-C18)	3	Starch esters	CO ₂	100-120°C; 1.5h; 100-150 bar	K ₂ CO ₃ (0.1)	0.034-0.348	65
6	Corn starch ^d	Lactic acid	0.9-9	Starch ester	CO ₂ +H ₂ O ^e	70-110°C; 1.5-9h; 70-300 bar	NaOH/Sn(oct) ₂ (0.39 ^f)	0.27-1.08 ^g	66

^a wt% of water present in the starch used is written in brackets. ^b molar ratio. ^c DS = degree of substitution; for entry 6, molar substitution (MS). ^d wt% of water was not given in the publication. ^e Water comes from the aqueous solution used to introduce lactic acid (20 wt%) and from the 0.40 M NaOH aqueous solution used to gelatinize starch. ^f NaOH/AGU molar ratio; Stannous 2-ethylhexanoate (Sn(oct)₂)/AGU ratio not given in the publication. ^g molar substitution (MS).

decrease its gelatinization temperature not only in the presence of added water (30-75 wt%)⁵⁵⁻⁵⁶ but also in the presence of the small amount of water contained in starch powder (16 wt%).⁵⁷ Moreover, the degree of gelatinization of a starch increased significantly in the presence of scCO₂, even at moderate pressure and temperature.⁵⁵⁻⁵⁷ This phenomenon would come from the ability of CO₂ to diffuse under pressure in the starch matrix and to act as a plasticizer.⁵⁸⁻⁵⁹ The dissolved CO₂ would so induce a swelling of the amorphous regions of starch, assisted by the available water, and would further lead to the disruption of the crystalline domains.⁵⁷ In term of reactivity, the resulting swelling of the starch granules makes the hydroxyl groups of amylose and amylopectin more accessible for a reactant⁶⁰ and thus facilitates the chemical functionalization.

Literature dedicated to functionalization of starch in densified CO₂ concerns almost exclusively esterification reactions (Table 2).

In 2010, Muljana et al. studied more closely the sodium acetate catalysed acetylation of potato starch by acetic anhydride in densified CO₂ (Table 2, entry 1).⁶¹ Different parameters (temperature, pressure, acetic anhydride to starch ratio, amount of catalyst and water content in starch) were varied to evaluate their influence on the substitution degree of the obtained modified starch but also on acetic anhydride conversion and reaction selectivity. The selectivity of the reaction was defined as the percentage of converted anhydride which has led to starch acetylation, the side reaction being hydrolysis of acetic anhydride in two molecules of acetic acid. In the used conditions (see Table 2, entry 1), a temperature increase had a positive influence on substitution

degree, conversion and selectivity. Conversely, decreasing the amount of water present in the used starch (15.2 wt%) had a bad influence on these three results. However, by doing comparative tests in water as solvent, the authors showed that the use of CO₂ gave much better results because of a too important competitive hydrolysis of acetic anhydride observed in water. Amounts of reactant and catalyst as well as pressure had only a slight influence on DS in the tested range (2-5/AGU, 0.1-0.8/AGU and 60-98 bar, respectively). Because of this slight influence of pressure, the authors concluded that the reported experiments were probably carried out at subcritical instead of supercritical conditions, the physical characteristics of the CO₂ as solvent being influenced when mixed with reactants and catalyst. Indeed, a discontinuity of the results should be observed around the critical point of the mixture and it seems that this critical point was not reached in the used conditions. Empirical models were also developed by the authors to rationalize the effects of the different parameters on the results. Concerning modified starch morphology, SEM images proved that acetylation reaction has led to granules agglomeration. Indeed, a partial fusion of starch granules was observed. This phenomenon would be due to the tendency of acetyl groups, grafted at low DS, to increase the global intermolecular hydrogen bonding.

The same authors have also published other works concerning the acetylation of potato starch in pressurised carbon dioxide and have shown that potassium carbonate was the best catalyst among those tested (K₂CO₃>Na₂CO₃>Na₂HPO₄>NaOAc>Mg(OAc)₂) (Table 2, entry 2).⁶² This superiority would come from its higher basicity. The highest

DS (0.96) was obtained after 24 h at 90 °C, under a pressure of 150 bar, with an acetic anhydride/AGU ratio of 4.35 and a K_2CO_3 /AGU ratio of 0.1. As described with sodium carbonate in their previous publication, Muljana et al. showed that temperature has the largest effect on the DS of the obtained starch acetate. Concerning the influence of pressure, the authors noted that, whatever the temperature or the potassium carbonate amount, the obtained DS showed a maximum at a pressure of about 150 bar, corresponding to the critical pressure of the mixture. The increase in DS observed when increasing the pressure under the critical pressure (subcritical region) would be due to an enhancement of the solubility of CO_2 in starch leading to an improvement of the acetic anhydride mass transfer into the starch matrix. Conversely, the decrease in DS obtained at higher pressure (supercritical region) would come from compressive effects which would lead to a reduction of the free starch volume and thus a decrease in the reactant mass transfer into starch. SEM pictures of the acetylated products showed a fusion of the granules at low DS (0.23–0.36) and a complete loss of the granular structure at higher values (0.62). DSC experiments showed decreasing glass transition temperatures (T_g) when the DS increased, showing that the starch chemical modification improved the chains mobility. TGA measurements demonstrated that initial degradation temperature of the acetylated starches synthesized in CO_2 was lower than that of native starch. Interestingly, aqueous suspensions of all products made in CO_2 exhibited lower viscosities than those determined for acetylated starches prepared in water and possessing the same DS. This result was interpreted by a higher extent of hydrogen bonds disruption for the samples synthesized in pressurised CO_2 .

The same team has also studied the sodium acetate catalysed acetylation of potato starch by acetic anhydride (see Table 2, entry 3 for experimental conditions).⁶³ Once again, the highest degrees of substitution were found near the critical pressure of the mixture (DS of 0.29 and 0.62 obtained after 1 and 24 h, respectively, at 150 bar). A broad pressure range (80–250 bar) was explored with a view-cell technology which allowed to determine that this critical pressure of the mixture increased from 94–100 bar to 145–148 bar when the temperature increased from 50 to 90 °C. By studying the acetylation of starch particles of different size obtained by fractionation with sieve trays, the authors also showed that a larger average particle size led to lower DS value, whatever the conditions (50 °C/80 bar and 90 °C/150 bar, *i.e.* in subcritical and supercritical conditions respectively). This result suggests that the mass transfer of the reactant inside the starch granules plays a determining role on the reaction kinetic in pressurised CO_2 .

Muljana et al. also studied the synthesis of starch esters from potato starch in supercritical CO_2 mainly using vinyl esters of fatty acids as reactants and a base as catalyst (Table 2, entry 4).⁶⁴ K_2CO_3 was the best catalyst among those tested with 3 eq. of vinyl laurate (C12) introduced per AGU: triethylamine, Na_2HPO_4 and NaOAc gave respectively a DS of only 0.01, 0.09 and 0.03 compared to a DS of 0.26 obtained with K_2CO_3 in the same conditions (150 °C, 150 bar, 18 h, 0.1 eq. of catalyst per AGU). Therefore, triethylamine gave the worse result and, among the mineral bases tested, higher activity of K_2CO_3 would be due to its higher basicity. As observed by the same authors with acetic anhydride in their previous works, the DS obtained with vinyl laurate is enhanced by higher temperatures and longer reaction times and showed a clear optimum by varying pressure, the optimal pressure being around 80 bar in the conditions used. The positive effect of the increase in pressure under 80 bar would be due to a plasticizing effect of $scCO_2$ in the starch matrix increasing the

diffusion rate of the reactant. Oppositely, the negative effect observed above 80 bar would come from a decrease in the reactant solubility in the starch because of compressive effects inside the starch granules. Vinyl butyrate (C4) and vinyl stearate (C18) were also tested and gave lower DS than vinyl laurate (respectively 0.19 and 0.06 instead of 0.26 in the used conditions: 150 °C, 150 bar, 18 h, 3 eq. of reactant per AGU, 0.1 eq. of catalyst per AGU). In the same conditions, butyric anhydride and stearic anhydride were less performant compared to the corresponding vinyl esters (DS of 0.08 vs 0.19 and 0.01 vs 0.06, respectively). These results were explained by the fact that vinyl alkoxide is a better leaving group than carboxylates. With the same potato starch, methyl esters (methyl caprylate (C4), laurate (C12) and oleate (C18:1)) were also tested but gave very low DS (0–0.004). These inferior results were justified by a stronger basicity of methoxide, indicating a low ability of it to be a good leaving group. A DSC study of the starch esters showed lower melting and crystallization temperatures compared with native potato starch. This result was explained by a reduction of crystallinity due to the esterification reaction. The first derivatives of TGA curves of the synthesized starch laurate samples exhibited two degradation peaks, respectively attributed to modified amylopectine (at low temperature) and to modified amylose (at higher temperature). Contact angle measurements demonstrated that starch laurate hydrophobicity increased from DS=0 to 0.15 and then slightly decreased (from DS=0.15 to 0.28). This paradoxical decrease in hydrophobicity was rationalized by assuming a plasticizing effect of the lauric chains on the starch matrices at higher DS, leading to a higher starch chains mobility.

In a more recent publication, Muljana et al. described the synthesis of sago starch esters by transesterification of fatty acid methyl esters (FAME) in densify CO_2 and with potassium carbonate as catalyst (Table 2, entry 5).⁶⁵ The influence of temperature was exactly the same than that described in their previous publications with acetic anhydride and vinyl esters, temperature increasing the reaction rate and leading consequently to a higher DS. Conversely, the influence of the pressure seemed more complex to understand and depended on the methyl ester used and on the temperature at which the experiment was conducted. As a matter of fact, the best results were obtained for the different reactants tested at 120 °C but at different optimal pressure: 150 bar for methyl laurate (C12) and methyl myristate (C14) (DS of 0.166 and 0.307 respectively), and 100 bar for methyl palmitate (C16) and methyl oleate (C18:1) (DS of 0.45 and 0.348 respectively) (see Table 2, entry 5 for other conditions). The fact that methyl esters as reactants gave much better results than those obtained by the same team with potato starch in similar conditions⁶⁴ was interpreted by a higher reactivity of sago starch compared to potato starch. Analysis of the starch esters samples by SEM showed undoubtedly an agglomeration behaviour of sago starch granules after reaction, whatever the graft nature. The TGA indicated that, for a same DS, a lower initial degradation temperature than that of native sago starch and decreasing with graft length. The glass transition temperatures determined by DSC followed the same evolution. This tendency was explained by an internal plasticizing effect of the fatty chains.

Piskin et al. have conducted the graft copolymerization of lactic acid (LA) onto starch in supercritical CO_2 to obtain starch esters bearing polylactic acid chains (Table 2, entry 6).⁶⁶ In this study, it is important to note that the used corn starch (5 g per experiment) was firstly gelatinized by 30 mL of 0.40 M NaOH (*i.e.* 0.39 eq. of NaOH per AGU) at 70 °C for 1 h before being stirred in supercritical CO_2 with L-Lactic acid (20 wt% aqueous solution) and stannous 2-ethylhexanoate

(Sn(Oct)₂) as catalyst. The results are presented by the authors in terms of grafted LA (mol%, *i.e.* number of moles of grafted LA units for 100 moles of "LA + AGU" units) obtained by varying starch/LA initial ratio (w/w). For better understanding, these results can be easily converted in MS (molar substitution degree, meaning number of lactic acid moiety grafted per AGU) as a function of number of molar equivalent of LA introduced per AGU at the beginning of the reaction. The obtained MS increases with temperature up to 100 °C and then decreases. According to the authors, this decrease would be due to the breaking of grafted LA and/or the tendency of LA to prefer homo-polymerization than grafting at higher temperature. At this optimal temperature of 100 °C and using 5.4 eq. of LA per AGU, the MS reaches the maximal value of 1.08 (*i.e.* 52 mol% of lactic acid and 48 mol% of AGU) after 6 h of reaction and then stabilizes. The used pressure of CO₂ was equal to 200 bar, a lower pressure giving lower results (MS = 0.75 at 100 bar and 0.27 at 70 bar) and a higher pressure having no incidence on the MS (MS = 1.08 at 300 bar as at 200 bar). Decreasing the amount of LA introduced per AGU at the beginning of the reaction led logically to a decrease in the MS (MS = 0.69 at 1.8 eq and 0.47 at 0.9 eq., instead of 1.08 at 5.4 eq.). However, increasing the amount of LA did not lead to a higher molar substitution, a lower MS of 0.75 being obtained at 9 eq. The PLA grafted starch material possesses a predominantly amorphous structure, as demonstrated by the disappearance of the characteristic crystalline peaks of native starch on the X-ray diffraction patterns. SEM permitted to observe dramatic changes in the morphology of the product, starch granules being completely destructured. Interestingly, TGA indicated that the graft copolymerization of lactic acid on the starch backbone led to an enhancement of its thermal stability.

3. Unconventional technologies for chemical modifications of starch

3.1 Chemical modifications of starch under microwave radiation

Microwave-enhanced chemistry is based on the efficient heating of materials by "microwave dielectric heating" effects. The use of microwave irradiation decreases the reaction time, increases the product yield and sometimes results in a different products distribution compared to conventional heating counterparts. Indeed, organic synthesis is traditionally performed by conductive heating with an external heat source. This is not an optimal method for transferring energy into the system, since it depends on the thermal conductivity of the various materials that must be penetrated. In contrast, microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture.⁶⁷ For example, microwave irradiation decreases the degree of crystallinity of wheat starch.⁶⁸ In this context, the effect of microwave radiation on the modification process of starch was studied (Table 3).

Methylation of cassava starch with dimethyl carbonate (DMC) and 5% sodium chloride aqueous solution as solvent can be achieved by employing disodium hydrogen phosphate (Na₂HPO₄), as a catalyst and by utilizing microwave heating (Table 3, entry 1).⁶⁹ In the absence of base, the DS was very low (DS=0.061). To minimize side reactions, a weak base such Na₂HPO₄ was chosen. The increase in the amount of Na₂HPO₄ or DMC favorably increased the DS. The influence of microwave time on the reaction was also investigated. The DS increased and then decreased along with the increase in

microwave time. The authors explained that a long microwave time could promote the decomposition of DMC into CO₂ and methanol by hydrolysis. A maximal degree of substitution of 1.087 can be reached with a microwave time of 12 minutes at a ratio DMC/AGU of 20 and Na₂HPO₄/AGU of 0.1. The authors concluded that the methylation with DMC under microwave irradiation was safe, nontoxic, environmentally friendly and suitable for industrial application. In addition, this process does not require inert and anhydrous conditions.

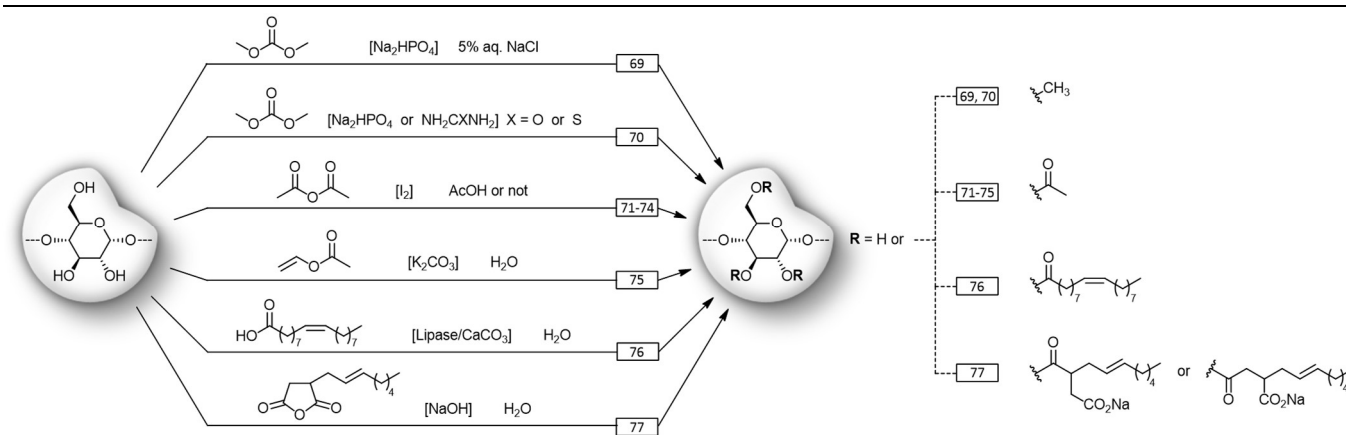
The same group worked on the same subject but using dimethyl carbonate (as reactant and as solvent) and employing disodium hydrogen phosphate (Na₂HPO₄), urea (NH₂CONH₂) or thiourea (NH₂CSNH₂) as a catalyst (Table 3, entry 2).⁷⁰ In the absence of base, nearly no methyl group could be detected (DS = 0.005). The efficiency of these bases in term of DS followed the order Na₂HPO₄<NH₂CONH₂<NH₂CSNH₂ (with DS = 0.028; 0.130 and 0.233, respectively). The best result obtained with NH₂CSNH₂ was explained by its higher alkalinity. With the NH₂CSNH₂ amount increase, the DS was firstly increased and then decreased. The same tendency was also observed for DMC amount. The decomposition of DMC by the base was suggested as an explanation. Finally, the effect of microwave time was investigated and the DS increased with microwave time up to 4 min. A methylated starch with a degree of substitution of 0.595 could be obtained with NH₂CSNH₂ and a microwave time of 4 min at a ratio DMC/AGU of 21 and NH₂CSNH₂/AGU of 0.22. Thermogravimetric analyses were performed on the native and methylated starches. In the case of methylated starches, decomposition began at lower temperatures. The XRD studies of methylated starches compared to native starch showed a loss of their semi-crystalline nature.

Acetylated starch can be obtained by employing acetic anhydride as an esterifying agent and using microwave assistance.^{71 72 73 74} The experiments were performed in pure acetic anhydride with or without acetic acid as additional solvent. In each case, iodine (I₂) was used as catalyst (Table 3, entries 3-6).

Sanchez-Rivera et al. studied the acetylation of banana and maize starch in pure acetic anhydride and with a microwave time of 2 minutes (Table 3, entry 3).⁷¹ The effect of different concentrations of iodine as catalyst was studied. Increase in iodine concentration led to higher DS. The higher degrees of substitution were equal to 0.214 and 0.519 in the case of banana and maize starch, respectively (Reactant/AGU of 4 and Catalyst/AGU of 0.05). SEM pictures of acetylated banana starch clearly revealed that the banana starch granules were more resistant towards modification than maize starch granules. The XRD studies showed that the acetylation decreased the crystallinity level in both starches. The acetylation decreased the plastic viscosity and starch retrogradation.

By activating corn starch with acetic acid and using acetic anhydride, Diop and coll. obtained starch acetate using microwave and iodine assistance (Table 3, entry 4).⁷² In a mixture acetic acid/ acetic anhydride of 1/1 (mol/mol), the experiment performed without iodine gave a corn starch with a DS equal to 0.25 with a microwave time of 2 minutes. An increase in the DS was observed with the increase in iodine concentration with a maximum of 2.934 (Reactant/AGU of 3 and Catalyst/AGU of 0.06). XRD measurements showed that the esterification processing destroyed the crystalline structure of the native starch. DSC analysis presented a relative reduction in the T_g with an increase in the DS. SEM results showed

Table 3 Chemical modifications of starch under microwave radiation (surrounded numbers in the scheme correspond to bibliographic references, column Ref. in the table)



Entry	Substrate	Reactants	Reactant / AGU ^a	Product	Solvent	Experimental conditions	Catalyst (Cata./AGU ^a)	DS	Ref.
1	Cassava starch	Dimethyl carbonate	8.7-26	Methylated starch	5% aq. NaCl	MW (1300 W); 5-20'	Na ₂ HPO ₄ (0.02-0.1)	0.033-1.087	69
2	Cassava starch	Dimethyl carbonate	13-25	Methylated starch	Dimethyl carbonate	MW (800 W); 1-5'	Na ₂ HPO ₄ , NH ₂ CONH ₂ or NH ₂ CSNH ₂ (0.001-0.015)	0.005-0.595	70
3	Banana or Maize starch	Acetic anhydride	4	Starch acetate	Acetic anhydride	MW (600 W); 2'; 100°C	I ₂ (0.01-0.05)	0.025-0.214 (B); 0.077-0.519 (M)	71
4	Corn starch	Ac ₂ O/AcOH	3	Starch acetate	Ac ₂ O/AcOH	MW (300 W); 2'; 100°C	I ₂ (0.06)	0.25-2.934	72
5	Corn starch	Ac ₂ O/AcOH	3	Starch acetate	Ac ₂ O/AcOH	MW (300 W); 2'; 100°C	I ₂ (0.018-0.06)	0.25-2.934	73
6	Sago starch	Ac ₂ O/AcOH	2-4	Starch acetate	Ac ₂ O/AcOH	MW (100 W); 2-10'; 100°C	I ₂ (0.0015-0.05)	0.016-1.26	74
7	Corn starch	Vinyl acetate	0.08-0.33	Starch acetate	H ₂ O	MW; 2.5-20'; 40-60°C	K ₂ CO ₃ (0.03-0.09)	0.049-0.131	75
8	Maize starch	Oleic acid	3.3-10	Starch oleate	H ₂ O	MW (700 W); 2'; 44°C, 4h	Staphylococcus aureus (SAL3); lipase (300-500 U)	1.55-2.86	76
9	Cassava starch	Octenyl succinic anhydride	0.02	Starch octenyl succinate	H ₂ O	MW (50 W); 10-60'	NaOH (pH = 9)	0.011-0.017	77

^a molar ratio.

that strong erosion occurred on the morphology of native corn starch after esterification. The water absorption index (WAI) and water solubility index (WSI) were increased with the DS and then started to decrease at value of 1.83 and 2.65, respectively. The authors claimed their products showed good thermoplastic and thermostable properties and were suitable for processing in non-food applications.

The same group performed similar experiments in a further publication (Table 3, entry 5).⁷³ Corn starch was pre-treated with acetic acid and then acetic anhydride under microwave irradiation in the presence of iodine. The iodine content, the temperature and the reaction time were fixed to limit the study of the effect of the molar ratios between acetic acid and acetic anhydride on the variation of the DS. From an acetic acid/acetic anhydride ratio of 2:1 to 1:1, an increase in the DS was observed. However, the DS decreased with the reduction of the molar ratio (1:1 to 0:1). The pretreatment with acetic acid could activate the reactive portions of starch molecule, which accelerated the esterification with acetic anhydride. Starch acetate with the highest degree of substitution (DS: 2.934) was obtained at a molar ratio of 1:1 (Reactant/AGU of 3 and Catalyst/AGU of 0.06). XRD patterns showed the extent of the

alteration of the initial crystallinity of corn starch after it was acetylated. Iodine played an important role in the destruction of the starch structure. DSC was used to determine that a net decrease in the glass transition could be seen after modification of starch occurred. The action of iodine was found to reduce the T_g of starch by reducing its molecular weight. The SEM micrograph demonstrated that the final acetylated product has undergone cleavage and helix extension causing breakdown of starch molecules into smaller portions. The change made in both WAI and WSI of modified starch was increased and followed by a decrease with the rising DS.

Starch acetate was prepared from sago starch by acetylating reaction, using iodine and microwave assistance (Table 3, entry 6).⁷⁴ The effect of four variables was studied: (i) the amount of acylation reagents, (ii) the ratio of acylating reagents (acetic anhydride/acetic acid), (iii) the amount of catalyst and (iv) the reaction time. A ratio of acylating reagents in favor of acetic acid and a long reaction time have a negative effect on DS. Therefore, acetic anhydride is a better acylating reagent and a longer reaction time may cause breakdown of starch acetate. The ratio of starch to acylating reagents was found to be important, but the amount of iodine was the most crucial factor. The amount of iodine has a positive effect on the DS. Iodine

has a great ability to absorb microwave to improve the reaction and shortens the reaction time. The highest DS was equal to 1.26 (acetic anhydride/acetic acid of 1:0; Reactant/AGU of 4; Catalyst/AGU of 0.05 and a reaction time of 10 min). The results of XRD analysis showed that acetylated starch had a more open structure compared to native. Starch acetates showed higher WAI and WSI in comparison to the native sago starch. The SEM results showed that aggregations and porosity on the surface of the acetylated starch granules increased with increasing DS.

Native corn starch was acetylated through the transesterification of vinyl acetate by a microwave assisted method using potassium carbonate as a catalyst in water (Table 3, entry 7).⁷⁵ The effects of the amount of catalyst, exposure time and reaction temperature on DS were explored. DS increased with increasing levels of K_2CO_3 and then decreased with further increase. The same behavior was observed with the exposure time and the reaction temperature since in the both cases a maximum DS was observed. Excess of base, exposure time or reaction temperature can induce the hydrolysis of acetylated starch and/or vinyl acetate leading to a DS decrease. The best DS was equal to 0.131 and was obtained after an exposure time of 12 minutes, a reaction temperature of 50°C (by microwave) and a ratio Reactant/AGU of 0.33 and a ratio of Catalyst/AGU of 0.06. The XRD results showed that native and acetylated starch have a similar pattern. Indeed, the crystallization degree of acetylated starch was slightly reduced. The acetylation reaction occurred mainly in the amorphous regions of the starch granules as confirmed by SEM experiments. Acetylated starch showed low viscosity compared to native starch. When acetylated, the rate of starch syneresis was reduced and a more fluid paste was obtained. The adhesion properties of acetylated starch increased with increasing DS. Yarns sized with acetylated starch had similar mechanical properties than PVP making it an ideal sizing agent for hydrophobic yarns.

A $CaCO_3$ -immobilized lipase from *Staphylococcus aureus* was used to catalyze the esterification reaction between oleic acid and maize starch using microwave heating (Table 3, entry 8).⁷⁶ The effects of three variables on the esterification efficiency were studied: (i) the reaction temperature, (ii) the amount of immobilized lipase and (iii) the starch/oleic acid molar ratio. The conversion yield dramatically decreased when increasing the temperature and with the increase of the starch/oleic acid molar ratio. High enzyme amount has also a negative effect. The optimal conditions to reach a degree of substitution of 2.86 are 386 IU of lipase, a ratio Reactant/AGU of 0.18 and an incubation of 2 minutes in a microwave-oven. After esterification, the starch exhibited an increase in viscosity. The increase in viscosity was linked to the increase of DS. DSC results showed that the esterification decreased the T_g . The hydrophobic starch fatty acid esters produced may have potential industrial applications such as surface coating, materials, flavoring agents in food industry and biomedical for bone fixation and replacements.

With cassava starch and octenyl succinic anhydride (OSA) as an esterifying agent, OSA-modified starch was prepared in aqueous alkaline solution (NaOH) with microwave assistance (Table 3, entry 9).⁷⁷ To maintain an appropriate temperature, water-bath heating or microwave radiation was used. The difference in the esterification reaction kinetics between starches treated with water-bath heating and microwave radiation were observed. The authors found that microwave radiation could reduce both the activation energy of the reaction and the pre-exponential factor. The higher DS was very low and equal to 0.017 for a ratio Reactant/AGU of 0.02 and a pH equal to 9. SEM images showed that the surface of starch granules in the

microwave field was destroyed more significantly than that in the water-bath heating.

3.2 Chemical modifications of starch by using ultrasonication

Ultrasonounds are high frequency waves (>20 kHz). When an ultrasonic wave propagates through a liquid, a compression of the liquid is followed by its expansion. Because of the pressure drop, small bubbles of gas are created. These bubbles grow with each cycle until they reach an unstable size where they collapse violently. This cavitation phenomena results in high local temperatures (4000 K) and pressure (1000 atm). Ultrasonication allows the creation of smaller particles in the case of solid-liquid medium (typically when metallic particles are used) leading to potentially higher rates of reaction. In liquid-liquid heterogeneous systems, the bubbles collapse at the interface, mixing the 2 phases and creating light emulsions. In the case of liquid medium only, the high energy of the implosion results in the weakening of covalent bonds leading to the creation of free radicals, especially when water is the medium. Specific reactions carried out under ultrasonic radiation can be accelerated or give other reaction pattern. The use of acoustic radiation has been since few years recognized by scientists as green methods for chemical activation. The cavitation collapse induced by the waves produce extreme conditions locally and conduce to the formation of new chemical species.

The impact of the ultrasonounds on physicochemical properties of starch was mainly studied.⁷⁸ Nevertheless, reactions of starch esterification and etherification with ultrasound assistance were described in the literature (Table 4).

Pretreatment of starch with ultrasonounds has been realized and the influence of this ultrasound pretreatment on the acetylation reaction has been studied by comparison of the DS obtained by the "ultrasound activated" starch and the one obtained with native starch (Table 4, entry 1).⁷⁹ The results showed that a higher DS value is always observed for the "ultrasound activated" starch under the same reaction conditions (1.8 vs 1.3). The crystallinity of the native starch was also always found to be destroyed as it was observed a partial gelatinization during the acetylation process. The authors also reported that ultrasound activation reduced the reaction time for acetylation.

For the reaction activated by ultrasonounds, influences of the molar ratio of catalyst/starch, reagent/starch, temperature, time and ultrasonication time on the DS of carboxymethyl modified cassava starch were studied (Table 4, entry 2).⁸⁰ The DS was greatly affected by the reaction time and by the sonication power. The highest DS

Table 4 Chemical modifications of starch by using ultrasonication (*surrounded numbers in the scheme correspond to bibliographic references, column Ref. in the table*)

Entry	Substrate	Reactants	Reactant / AGU ^a	Product	Solvent	Experimental conditions	Catalyst	DS	Ref.
1	Dioscorea Starch	Acetic anhydride	Not given	Starch acetate	Acetic acid	US (100 W); 75°C; 105'	H ₂ SO ₄	1.3-1.8	79
2	Cassava Starch	Monochloro acetic acid	0.75-1.5	Starch ether	H ₂ O/ EtOH	US (180-500 W); 35-55°C; 80'	NaOH	0.3-1.3	80
3	Cassava Starch	Monochloro acetic acid	0.1-0.3	Starch ether	H ₂ O/ EtOH	US (0-1000 W); 35°C; 1.5-6h	NaOH	0.36-1.15	81
4	Maize Starch	Octenyl succinic anhydride	0.1-0.3	Starch octenyl succinate	H ₂ O	US (400 W); 40-80°C; 30-120'	K ₂ CO ₃	0.007-0.027	82

^a molar ratio.

(1.23) was obtained for an ultrasound power of 500W and a reaction time of 15 min. The molar ratio of the catalyst (NaOH) had also a great influence on the DS, the maximum being reached with a molar ratio of 3.5. However a higher ratio decreased the DS as the reagent (Monochloroacetic acid) is in this case consumed by NaOH.

The effects of the US on the physicochemical properties of the carboxymethyl modified starch synthesized were also studied (Table 4, entry 3).⁸¹ It was shown that ultrasonic irradiation was a good way to prepare nano-sized carboxymethyl starch. The SEM images showed that the size of the particles after modification were much smaller (100-400 nm) than that of native starch particles. The nano-sized modified starch had enhanced solid dispersion properties of pharmaceutical drugs and also improved the solubility of poor water-soluble molecules.

Esterification under ultrasound irradiation was also studied with OSA as reagent (Table 4, entry 4).⁸² The use of ultrasonic treatment during octenyl succinylation resulted in a time reduction and an improvement of the efficiency of the reaction over the control over 15-20%.

3.3 Chemical modifications of starch by using ball-milling

Mechanochemistry is a technology that is used to directly transfer mechanical energy onto chemical systems by forces such as compression, shear, or friction. The mechanical energy generated by grinding two solids or a solid and a liquid substance breaks the order of the crystalline structure, leading to the formation of products. As such, mechanochemical activation could be a substitute to thermal means to promote chemical reactivity as molecular transformations are generated through mechanical forces.^{83 84 85} Recently, mechanical activation was also considerably reported in synthetic organic chemistry, in line with the development of green methodologies. Indeed, mechanochemical process appears to be a good and safe activation method to make chemical process greener as it can be an alternative to the use of hazardous solvent and also reduce the use of energy.⁸⁶

Even if this technology is now well documented, mechanochemistry is mainly used for decreasing the crystallinity of the starch granules and get amorphous starch, changing the starch properties.^{87 88} However, chemical modification of starch with mechanochemical activation recently appears in the literature.

As it is resumed in the Table 5, esterification reactions had been tested to evaluate the influence of the mechanical activation compare to the traditional methods. Ester modifications of starch with mechanical activation were not directly dependent on the nature of the starch and of the esterification agent as the degrees of substitution obtained in all cases are similar (0.015-0.041). Influences of the reaction time, catalyst concentration and reagent ratio were studied. No general tendencies can be risen for the substitution degree or the efficiency of the reaction. The variation depend on the mechanical activation type, catalyst and reagents ratio used. For the starch modification with octenyl succinic anhydride, two different catalysts have been tested, NaOH solution (Table 5, entry 1)⁸⁹ and sodium carbonate (Table 5, entry 2).⁹⁰ In both cases the reaction time is relatively short to get a maximum DS (0.029-0.039), 90 min with Na₂CO₃ and less than 10h for NaOH (0.9%) as catalyst. In both case, the authors have observed changes in modified starch due to the damage of the crystalline structure compare to native or traditional modified starch. The mechanochemical OSA starch exhibited a significantly lower temperature of gelatinisation determined by DSC analysis. The changes in the crystalline structure also increased the

Table 5. Chemical modifications of starch by using ball-milling (surrounded numbers in the scheme correspond to bibliographic references, column Ref. in the table)

Entry	Substrate	Reactants	Reactant / AGU ^a	Product	Solvent	Experimental conditions	Catalyst (Cata./AGU ^a)	DS	Ref.
1	Waxy rice starch	Octenyl succinic anhydride	0.004	Starch octenyl succinate	Water	2-70h	NaOH (0.001-0.011)	~0.02	89
2	Cassava Starch	Octenyl succinic anhydride	0.1-0.3	Starch octenyl succinate	-	60°C 30-120'	Na ₂ CO ₃ (0.002-0.3)	0.029-0.039	90
3	Cassava Starch	Lauric acid	0.1-0.3	Starch laurate	-	40-80°C 30-120'	K ₂ CO ₃ (0.005-0.065)	0.015-0.042	91
4	Waxy rice starch	Octenyl succinic anhydride	0.012-0.17	Starch octenyl succinate	Water	30°C 3-50 h	NaOH (nd)	0.005-0.028	92

^a molar ratio.

solubility in cold water, transparency, the emulsion stabilisation, the reduction of the paste viscosity and retrogradation. For esterification with lauric acid as reagent, different molar ratios of reagent and catalyst were tested (Table 5, entry 3).⁹¹ The best result (DS = 0.042) was obtained with a molar ratio of lauric acid /AGU of 0.5 and a mass ratio of K₂CO₃/starch of 0.025 and after a reaction time of 1h. Compared to conventional activation, the main changes were due to the structural disruption of the starch granules created by breakages and amorphization under mechanical activation. This phenomenon was proved by XRD analysis. These structures changes obtained by mechanical treatment gave different physicochemical properties (rheological, swelling and emulsifying) (Table 5, entry 4).⁹²

4. Conclusion

Our literature survey on the period 2010-2016 shows that unconventional media (ILs, scCO₂) and unconventional technologies (microwaves, ultrasounds and ball-milling) are increasingly investigated for starch etherification and esterification. It is in this way, that starch ethers and esters can be synthesized from native starch with DS values ranging from very low (~ 0.01) to high (~ 3). As mentioned in introduction, typical industrial processes are run to aim at DS below 0.4. These modification paths lead to modified starches bearing functional moieties essentially in amorphous parts of granule. The alternative media and technologies mentioned in this review can lead either to different DS or/and to different substitution pattern onto the polysaccharide backbone.

ILs were valuable solvents for functionalization on a wide range (DS up to 2.9). In scCO₂, only esterification reactions were described. Starch esters with a maximal DS around 1 were synthesized. By using microwave heating, starch ethers and esters can be synthesized with high DS (up to 2.9 for both). Starch esters have been synthesized with the assistance of ultrasound irradiation and DS up to 1.8 were reached. Mechanochemistry was mainly used to decrease the crystallinity of the starch granules. Nevertheless, chemical

modifications of starch appeared in the literature but in all cases, the DS were very low (< 0.04).

It is very difficult to compare the results presented since the solvents, the techniques of synthesis, the temperatures, the stirrings, the pressures, the concentrations and the kinds of starch are often different. Nevertheless, some comments can be addressed concerning each medium or technology.

The main advantage of ILs compared to classical solvents is its powerful dissolving capability, owing to the homogeneous modification of the native starches compared to the heterogeneous one usually observed. In ILs, the starch crystalline structure is broken rendering the hydroxyl groups more accessible for the reactant. The recyclability of some ILs was evaluated with success.

scCO₂ was able to diffuse in the starch matrix and led to the disruption of the crystalline domains, facilitating the chemical functionalization.

The reactions assisted by microwave or ultrasound irradiations are faster than reactions conventionally heated.

Mechanochemistry is of interest for specific applications requiring low DS and offers the advantage to work without solvent.

Concerning the market application, low DS can find various applications in food formulation, film forming, binding, adhesion thickening, stabilizing and texturing whereas higher DS can be used for their specific physico-chemical properties such as solubility, thermoplasticity, hydrophobicity and other applications such as hot melt adhesives, coating, cigarette filters, biodegradable packaging materials and pharmacy.²⁹

Depending on the targeted starch, this tutorial review aims to help researchers seeking an alternative medium or technology to functionalize starch with a specific DS.

In order to aware the researchers about each medium or technology, the Table 6 gathered their main advantages and drawbacks compared to conventional medium or technology.⁹³ Briefly, ILs possess high dissolving capability for starch, non-volatility, high modularity (combination choice for cation and anion) and large working temperature range (- 40°C to 200°C). The main

Table 6. Advantages and drawbacks of unconventional medium or technology compared to conventional medium or technology

Medium/Technology	Advantages	Drawbacks
ILs	Dissolving capability of starch, non-volatility, high modularity, large working temperature range.	Cost, potential toxicity, not always recyclable, potential reactivity with reactants, impurities.
scCO₂	Recyclability, non-toxicity, non-flammability, easy removal, inertia, ability to facilitate reaction by diffusing in the starch matrix.	Necessity to work under pressure, potential subsequent purification, cost of apparatus at industrial level.
Ultrasonication Microwave	Reduction of reaction time.	Cost of apparatus at industrial level, temperature homogeneity.
Mechanochemistry	Reduction of reaction time, absence of solvent.	Cost of apparatus at industrial level, potential subsequent purification.

drawbacks of ILs are high cost, potential toxicity (possibility of hydrogen fluoride formation with BF₄⁻ and PF₆⁻ as counter-anions), not always recyclable, potential reactivity with reactants and presence of potential impurities. The use of green equivalents of ILs, such as deep eutectic solvents (DESSs), could be an alternative. Indeed, some DESSs have already been used to plasticize starch⁹⁴ but up to now, no chemical modification of starch in DESSs was described in the literature.

The main advantages of scCO₂ are its recyclability, its non-toxicity, its non-flammable nature, its easy removal, its inertia toward acylating or alkylating reagents of starch (compared to water that can hydrolyse them), its ability to facilitate reaction by diffusing under pressure in the starch matrix. The main drawbacks of scCO₂ are the necessity to work under pressure (at least 74 bar), a subsequent purification with solvents is often necessary in the case of incomplete transformation and the cost of apparatus at industrial level.

The reactions assisted by ultrasonication or microwave are generally performed with a shorter period of time, but the cost of apparatus at industrial level could be a disadvantage due to the use of a specific reactor (ultrasonication or microwave) or the erosion of the probe (ultrasonication). Note that in the case of a heterogeneous system, the temperature is not always uniform.

The mechanochemistry offers the advantage to work without solvent and for shorter period of time. Nevertheless, the cost of apparatus at industrial level could be a problem with the use of a specific reactor or a rapid erosion of bowls and balls. In addition, a subsequent purification with organic solvents can be necessary to recover the products of reaction.

So, to implement the results obtained with these technologies or media at the lab scale to pilot scales applications, it is necessary to pay attention of the economical aspects. The cost of manufacturing (apparatus and energy consumption) using these technologies or media has to be studied in relation with the prices of the targeted products. Indeed, it can be a significant brake on market development for the production of low value chemicals. Nevertheless, the aim is to use the greenness of these technologies or media according to the required characteristics of starch, market trends and cost.

Finally, another point seems important to underline. Indeed, for each unconventional technology, a modification of morphology and a loss of crystallinity for starch were generally observed by XRD or SEM. In addition, thermal analysis showed a decrease in the degradation temperature. Even if it is not always mentioned in the publications, the use of microwaves, ultrasounds or ball-milling can generate local high temperature or local high pressure probably leading to a partial

degradation of starch molecular structure. Indeed, high microwave energy induced depolymerization of starch to glucose.³² Harsh acidic conditions can appear in the case of acidic ILs and CO₂ as solvents. These drastic conditions probably also lead to a degradation of starch molecular structure. Therefore, it seems essential to pay a particular attention to the potential degradation of starch. Unfortunately, this point has not hardly ever been discussed in these publications although this information is full of interest.

To resume, the scale-up and the economic aspects of these new processes need to be more investigated for further developments. Furthermore, it is sure that exciting challenges remain to be reached such as the coupling of unconventional media and technologies to favor new processes.

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