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# Solvent-free fatty acylation of cellulose and lignocellulosic wastes.

## Part 2: reactions with fatty acids<sup>1</sup>

C. Vaca-Garcia, M.E. Borredon\*

Laboratory of Agro-Industrial Chemistry (Associated INRA unit 31A1010) ENSCT, Institut National Polytechnique de Toulouse, F-31077 Toulouse Cedex 04, France

### Abstract

The mixed acylation of cellulose with fatty acids and acetic anhydride was accomplished in an excess of fatty acid, thus avoiding the addition of a toxic solvent. The experimental design enabled the parameters of a model reaction with octanoic acid to be optimized. The products contained both acetyl and octanoyl acyl groups in a 2.4/1 ratio and the maximum degree of substitution (DS) was 2.2. The use of fatty acids higher than C<sub>8</sub> resulted in a decrease of the DS. The model reaction was applied to the esterification of four lignocellulosic wastes (LW). Their reactivity was comparable to that of cellulose when no pretreatment was used. A solvent-exchange pretreatment improved the acylation of LW by about 60%, whereas that of cellulose was increased by more than 400%. The hydrophobic character of the esterified products was confirmed.

**Keywords:** Cellulose esterification; Mixed esters; Solvent-free techniques; Fatty acids; Acetic anhydride; Lignocellulosic wastes; Pine sawdust; Wheat straw; Olive stones; *Agave tequilana* (Weber)

### 1. Introduction

Cellulose derivatives are readily synthesized when a cellulose solvent is used. The crystalline structure of the biopolymer is destroyed, resulting in the maximum accessibility of its hydroxyl groups. The cellulose solvents used for chemical modification are usually binary systems composed of a salt and an aprotic solvent, e.g., lithium chloride/dimethylacetamide (LiCl/DMAc) (Johnson, 1985) or tetraethyl ammonium chloride/dimethyl sulfoxide (Kamata et al., 1985). The ecological impact and the price of such compounds limit their utilization to a laboratory scale and demand that research groups develop alternative free-solvent techniques.

When no cellulose solvent is used in the chemical modification of cellulose, cellulose reactivity is severely decreased. Indeed, the accessibility of the reactive sites is reduced due to the intermolecular and intramolecular hydrogen bonds between hydroxyl groups. This limita-

tion can be reduced in two ways. First, by using a cellulose-swelling organic compound that can break some of the intermolecular hydrogen bonds in cellulose. These compounds are proton acceptors of low molecular weight such as dimethylformamide (DMF), pyridine or dimethyl sulfoxide (Robertson, 1970). However, the toxicity of such swelling compounds is comparable to that of the cellulose solvents. The second alternative is the use of a dispersing agent in which the cellulose derivative dissolves progressively as the reaction advances. Thus, the hidden hydroxyl groups become accessible as a result of the "peeling" of cellulose. This strategy has been successfully applied in the industrial production of cellulose acetate and other short aliphatic ( $\leq C_4$ ) cellulose esters (Serad and Sanders, 1979). In this case, the corresponding carboxylic acid, which is relatively inexpensive and innocuous, is used as a dispersing agent. Even if the solid dissolves in the dispersing agent, we refer to such techniques as "solvent-free" since the dispersing agent is intrinsically present in the reaction medium (i.e., as a reagent or a product) and it is not a toxic added solvent.

Concerning the production of long aliphatic (fatty) cellulose esters, few attempts have been made to facilitate production scale-up. Cellulose fatty esters are usually prepared from fatty acid chlorides in a pyridine-DMF

\* Corresponding author. Tel.: +33-5-6117-5724; fax: +33-5 6117-5730; email: lcacatar@cict.fr

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medium. In previous works (Thiebaud and Borredon, 1995; Kwatra et al., 1992), the fatty acylation of cellulose and wood without these solvents was achieved. Such efforts are only partially successful because acid chlorides are relatively noxious and they produce hydrochloric acid during acylation reactions. Other methods of fatty esterification combine the use of a fatty acid and a co-reagent. The latter reacts in situ with the fatty acid to form a more reactive entity capable of grafting the fatty chain to cellulose. These co-reagents are toxic compounds such as trifluoroacetic anhydride (Arni et al., 1961), tosyl chloride (Shimizu and Hayashi, 1989), mesyl chloride (Talaba et al., 1996) or dicyclohexylcarbodiimide and pyrrolidinopyridine (Samaranayake and Glasser, 1993).

In a recent work (Vaca-Garcia et al., 1998), the use of acetic anhydride as a non-toxic co-reagent of fatty acids to synthesize cellulose mixed acetic-fatty triesters was reported (Fig. 1). The study of the reaction mechanism was carried out with cellulose previously dissolved in LiCl/DMAc. The mixed cellulose esters showed good hydrophobic and mechanical properties. In the present work, we proposed to simplify this technique by eliminating the cellulose solvent and to apply it to the acylation of lignocellulosic residues. Cellulose was pretreated by the solvent-exchange technique and the fatty acid was used in excess as a dispersing agent.

In the first part of this report, the investigation of a solvent-free model reaction using cellulose and octanoic (caprylic) acid is described. The generalization of this reaction to other higher linear fatty acids and the application of the optimized model reaction to four lignocellulosic wastes (LW) obtained from agro-industrial factories is then presented. The selected LW were: pine sawdust and wheat straw, which are common

vegetal residues, as well as olive stones and bagasse of agave (*Agave tequilana* Weber), which are non-utilised residues produced in considerable amounts from the industrial production of olive oil and tequila.

## 2. Methods

**Materials.** Reagent grade chemicals were purchased from Aldrich France and were used without further purification. Alpha cellulose (4% pentosans) was furnished by Sigma France. The characteristics of the LW are presented in Table 1.

**Solvent-exchange pretreatment.** Two grams (dry basis) of cellulose or LW were stirred in 200 ml of deionized water for 5 min then filtered over fritted glass. The swollen substrate was washed on the filter with ethanol then twice stirred in 80 ml of ethanol for 5 min and filtered each time. The solid was washed on the filter with fatty acid (the same as used in the acylation reaction) at a temperature 20°C above the melting point of the fatty acid, then stirred twice in 80 ml of fatty acid for 10 min at the same temperature and filtered each time.

**Acylation reaction.** A mixture composed of fatty acid (5.6 eq/cellulose OH), acetic anhydride (2 eq/OH) and H<sub>2</sub>SO<sub>4</sub> catalyst (3–7 meq/OH) was heated at 90°C for 1 h. Solvent-exchanged cellulose (2.0 g dry basis) was added to the reaction medium. The whole mixture was stirred at 110–130°C for 1–3 h. At the end of the reaction, 150 ml of ethanol were added to precipitate the solubilized fraction. The solid was separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then dried at 105°C to constant weight. The same procedure was used with LW and the amounts of reagents were calculated as if the substrate was cellulose.

**Degree of substitution (DS).** The fatty acyl and acetyl groups in cellulose mixed esters were determined using the reported aminolysis method (Mansson and Samuelson, 1981) in which the ester groups are split by reaction with pyrrolidine and the acyl amides formed are quantified by gas chromatography.

**Ester content (EC).** One gram of pulverized sample was stirred for 30 min in 40 ml of aqueous ethanol (70%). After addition of 40 ml of a 0.5N NaOH aqueous solution, the stirring was continued for 48 h at 20°C. The unreacted NaOH was back-titrated with 1N aqueous HCl. The solid was recovered by filtration and thoroughly washed with deionized water and ethanol, then dried at 50°C for 48 h. The absence of ester functions in the saponified solid was confirmed by FTIR spectroscopy. The EC was calculated as the number of equivalents of reacted NaOH per gram of sample.

**Degree of polymerization (DP).** The cellulose mixed esters were saponified in mild conditions (as in EC determination, above) to regenerate cellulose. The intrinsic

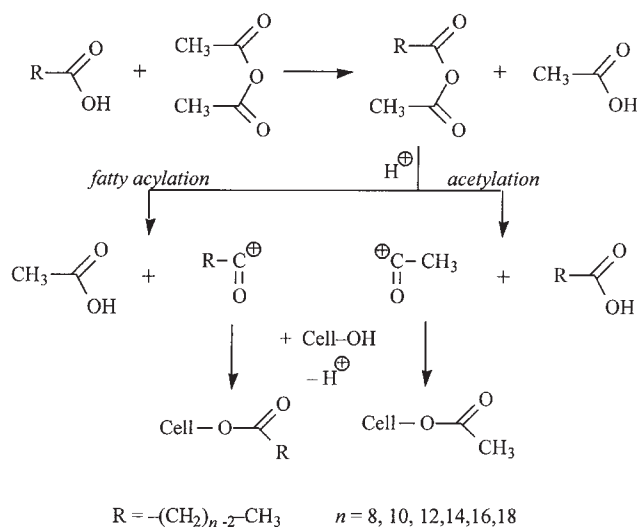


Fig. 1. Mechanistic scheme of the mixed esterification of cellulose with a fatty acid and acetic anhydride.

Table 1

Characteristics and composition (dry basis, extractibles free) of lignocellulose wastes (LW) determined according to the ADF-NDF method (Van Soest and Wine, 1967), ASTM standard D1106-84 and Tappi standard T 211 OM-03

Substrate	Particles size	Extractibles (%) <sup>a</sup>	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
Pine sawdust	2–10 mm	5	47	23	29	0.5
Wheat straw	5–20 mm	11	42	35	16	5.2
Olive stones	100–200 mesh	22	70	22	5	0.8
Agave bagasse	60–80 mesh	10	50	23	18	6.0

<sup>a</sup> In Soxhlet extractor with toluene-ethanol 50:50 v/v for 8 h, then with ethanol for 8 h.

viscosity ( $\eta$ ) of diluted solutions of cellulose in cupriethylenediamine was measured at 25°C with a capillary viscometer according to the French AFNOR standard NF T 12-005. The DP was calculated using the Mark-Houwink-Sakurada equation (Brandrup and Immergut, 1975) which correlates  $\eta$  and the viscosimetric molecular weight ( $M_v$ ) of cellulose:

$$DP = M_v/162 = ((\eta/0.0133) \wedge (1/0.905))/162,$$

where 162 is the molecular weight of the anhydroglucose monomer, 0.0133 and 0.905 are the coefficients corresponding to the cupriethylenediamine system and  $\eta$  is expressed in ml/g. Blanks were also carried out to evaluate the reduction in DP due to the saponification. A decrease of 10% was detected and the measured values were thus corrected.

*Weight increase (WI) and recovery yield (RY).* The precipitated product was weighed ( $W_p$ ) after purification and the WI was calculated as:

$$WI(\%) = 100 \times (W_p - W_o)/W_o,$$

where  $W_o$  is the weight of initial cellulose or LW. The non-precipitated part was estimated by assuming that its DS was the same as that of the precipitated fraction. Thus, the RY was defined as the ratio of the precipitated fraction to the theoretical total product given by the equation below:

$$RY(\%) = 100 \times \frac{W_p}{W_o \times \left( \frac{162 + DS_2(43-1) + DS_n(MM_n-1)}{162} \right)},$$

where  $DS_2$  and  $DS_n$  are the DS of the acetyl and the fatty acyl substituent and  $MM_n$  is the molecular weight of the fatty acyl substituent (127 for the octanoyl).

*Experimental design.* We used the least-squares method to determine the coefficients  $\beta_0$ ,  $\beta_i$  and  $\beta_{ij}$  of a second-order polynomial model, which linked a studied response  $R$  to the normalized values,  $X_i$ , of three factors:

$$R_n = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} X_i X_j,$$

where  $X_i = (U_i - U_i^o)/\Delta U_i$ ;  $U_i$  = actual variable,  $U_i^o$  = actual variable at the center of the experimental domain, and  $\Delta U_i$  = the variation step of each variable.

*Static contact angle measurements.* Disks (10 mm diameter) of the esterified products were obtained by using a laboratory press (10 ton) and a conventional pellet mold. A water drop (2  $\mu$ l) was placed on the surface of

the disk. For each sample, a picture of the magnified drop was taken. The tangent line to the drop was drawn on the picture to measure the contact angle. Four disks were made for each sample.

### 3. Results and discussion

#### 3.1. Solvent-free model reaction

On a model reaction between cellulose and octanoic acid with acetic anhydride co-reagent, the effects of three variables: the sulfuric acid catalyst concentration ( $C$ ), the temperature ( $T$ ) and the time ( $t$ ) of reaction were studied. A central composite experimental design was used to evaluate their simultaneous interaction on the DS, the DP, the WI and the RY of the solid product. Preliminary experiments suggested that the experimental domain be confined to the following ranges:  $T = 110$ – $130^\circ\text{C}$ ,  $t = 1$ – $3$  h and  $C = 3$ – $5$  meq/OH. The matrix of experiments and results is presented in Table 2.

In a previous work (Vaca-Garcia et al., 1998), it was demonstrated that the mixed esterification technique does not consist of two independent acylation reactions. When acetic anhydride is not added, the fatty acid reacts with cellulose only in extremely low yields. The acetylation reaction is favored since the acetylum ion ( $\text{CH}_3\text{C}^+\text{O}$ ) has a larger electronic deficit and a smaller size than the octanoylium ion ( $\text{C}_7\text{H}_{15}\text{C}^+\text{O}$ ). The acetate/octanoate ratio in a cellulose solvent medium was found to be 2.7, which is not significantly different from the value obtained in the solvent-free experiments of Table 2 ( $2.4 \pm 0.3$ ). It seems that the absence of cellulose solvent does not interfere with the dissociation of the mixed anhydride. Furthermore, the narrow range of variation of this ratio indicates that the selectivity of acylation is little dependent on the reaction conditions.

The experiment at the center of the experimental domain ( $120^\circ\text{C}$ , 2 h, 5 meq/OH) was replicated four times to evaluate the experimental uncertainty of each response ( $s_{DS}^2 = 0.0014$ ,  $s_{WI}^2 = 5.58$ ,  $s_{RY}^2 = 0.67$ ,  $s_{DP}^2 = 304.7$ ). The coefficients of the second-order equation for every response are presented in Table 3. The statistical significance of every parameter was measured by the  $t$ -test with 8 degrees of freedom. The statistical significance of every mathematical model was evaluated

Table 2

Experimental design for the mixed esterification reaction of cellulose with octanoic acid and acetic anhydride.  $DS_8$  = degree of substitution with the octanoyl group,  $DS_2$  = degree of substitution with the acetyl group, WI = weight increase, DP = degree of polymerization, RY = recovery yield

$T$ { $X_1$ } (°C)	$t$ { $X_2$ } (h)	$C$ { $X_3$ } (meq/OH)	$DS_8$	$DS_2$	$DS_{total}$	WI (%)	DP <sup>b</sup>	RY (%)
110 {−I} <sup>a</sup>	1 {−I} <sup>a</sup>	3 {−I} <sup>a</sup>	0.07	0.19	0.26	8	404	98
130 {+I}	1 {−I}	3 {−I}	0.10	0.25	0.35	18	299	100
110 {−I}	3 {+I}	3 {−I}	0.08	0.21	0.29	9	450	98
130 {+I}	3 {+I}	3 {−I}	0.10	0.27	0.37	18	287	100
110 {−I}	1 {−I}	7 {+I}	0.26	0.76	1.02	32	215	95
130 {+I}	1 {−I}	7 {+I}	0.69	1.31	2.00	−7	100	50
110 {−I}	3 {+I}	7 {+I}	0.41	0.80	1.21	57	136	100
130 {+I}	3 {+I}	7 {+I}	0.76	1.42	2.18	−41	100	30
110 {−I}	2 {0}	5 {0}	0.31	0.83	1.14	45	238	100
130 {+I}	2 {0}	5 {0}	0.66	1.47	2.13	45	189	76
120 {0}	1 {−I}	5 {0}	0.27	0.66	0.93	33	130	97
120 {0}	3 {+I}	5 {0}	0.34	0.75	1.09	48	174	100
120 {0}	2 {0}	3 {−I}	0.10	0.22	0.32	12	330	99
120 {0}	2 {0}	7 {+I}	0.41	0.94	1.35	44	138	92
120 {0}	2 {0}	5 {0}	0.25	0.66	0.91	31	190	96
120 {0}	2 {0}	5 {0}	0.23	0.64	0.87	28	223	95
120 {0}	2 {0}	5 {0}	0.29	0.67	0.96	33	183	95
120 {0}	2 {0}	5 {0}	0.26	0.66	0.92	33	200	94

<sup>a</sup> The numbers in brackets indicate the level of the coded variable  $X_i$ .

<sup>b</sup> DP of the starting  $\alpha$ -cellulose = 972.

Table 3

Coefficients  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ij}$  of the second order polynomial model for each four studied responses. The level of confidence (evaluated by the  $t$ -test) is indicated in parentheses for the parameters whose statistical significance is lower than 99%. See Table 2 for abbreviations

Coefficient	Studied responses			
	$DS_{total}$	WI	RY	DP
$\beta_0$	1.05	38.7	96.5	190
$\beta_1$	0.31	−11.8	−13.5	−47
$\beta_2$	0.06	0.7 (62.4%)	−1.2	0 (1.4%)
$\beta_3$	0.62	2.0 (97.2%)	−12.8	−108
$\beta_{12}$	0.00 (14.7%)	−7.5	−3.1	3 (31.8%)
$\beta_{13}$	0.22	−19.5	−14.9	15 (95.5%)
$\beta_{23}$	0.04 (98.4%)	−1.3 (82.7%)	−1.9	−14 (94.9%)
$\beta_{11}$	0.46	−1.2 (57.3%)	−10.1	33 (98.5%)
$\beta_{22}$	−0.17	−5.7	0.4 (56.2%)	−29 (97.4%)
$\beta_{33}$	−0.34	−18.2	−2.6	53
<i>Model's</i>				
<i>confidence level</i>				
( $F$ -test)	99.5%	99.7%	99.9%	85.7%

by the  $F$ -test ( $F_{5,3}$  = uncertainty due to the lack of fit/experimental uncertainty). The contour plots of the Fig. 2 polynomial equations are presented in Figs. 3–6.

Above a certain concentration, the sulfuric acid catalyst can break the glucosidic bonds in the cellulosic polymer, especially at high temperatures. Thus, low molecular products may be formed as esterification proceeds. Since these oligomers cannot precipitate if their DP is lower than a critical DP value, a fall in the RY of the solid product may be observed, as represented schematically in Fig. 2. Hence, we first investigated the evolution in time of the average DP of the precipitated solid (Fig. 3). After 3 h of reaction, the DP can fall

below 150 in a relatively wide zone of  $T$ – $C$  values, and even fall below 100 (the minimum DP in commercial cellulosic products) under the most severe conditions. However, after 2 h of reaction, the product maintained a DP higher than 100 in the whole  $T$  and  $C$  domain. Since the DP-mathematical model was significant only at the 86% level of confidence, we considered it useless to estimate the exact time at which the DP falls below 100. The effects of  $T$  and  $C$  on the  $DS$ ,  $WI$  and  $RY$  were therefore studied at  $t = 2$  h. Recovery yields of almost 100% (i.e., minimal depolymerization) could be obtained if at least one of the two variables,  $T$  or  $C$ , was kept at its lowest value (Fig. 4). The line  $RY = 95\%$  will delineate



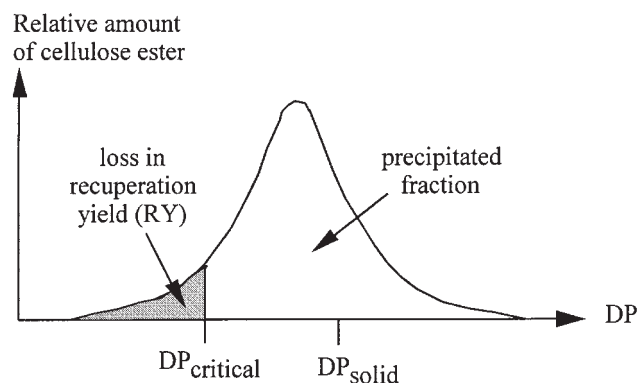


Fig. 2. Schematic representation of the degree of polymerization distribution of the acylated cellulose after reaction. Only the molecules with a DP higher than  $DP_{critical}$  can be recovered by precipitation.

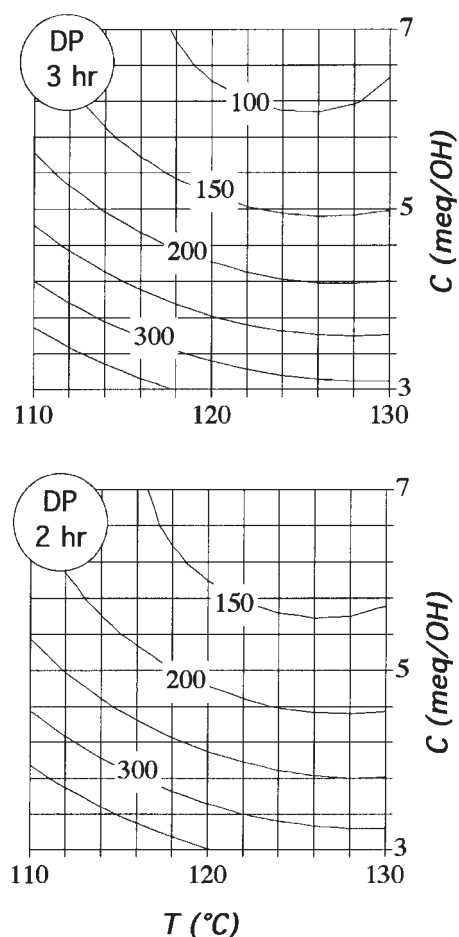


Fig. 3. Isoresponse curves for the degree of polymerization (DP) of cellulose after 2 and 3 h of acylation with octanoic acid and acetic anhydride as a function of the temperature ( $T$ ) and the  $H_2SO_4$  catalyst concentration ( $C$ ).

the most convenient operation range for an economically feasible process.

On the other hand, after 2 h of reaction, the DS values spread from 0.3 to 2.2 (Fig. 5). The maximum DS

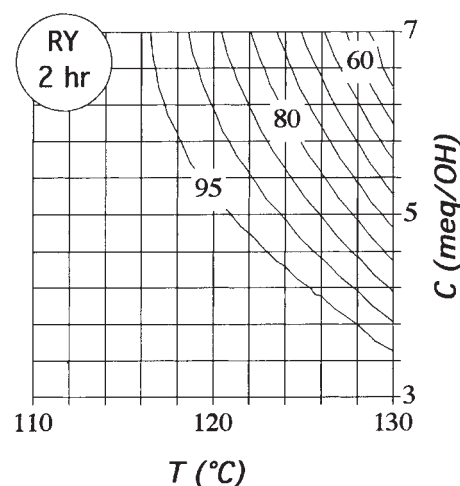


Fig. 4. Isoresponse curves for the recovery yield (RY) of cellulose ester after 2 h of acylation with octanoic acid and acetic anhydride as a function of the temperature ( $T$ ) and the  $H_2SO_4$  catalyst concentration ( $C$ ).

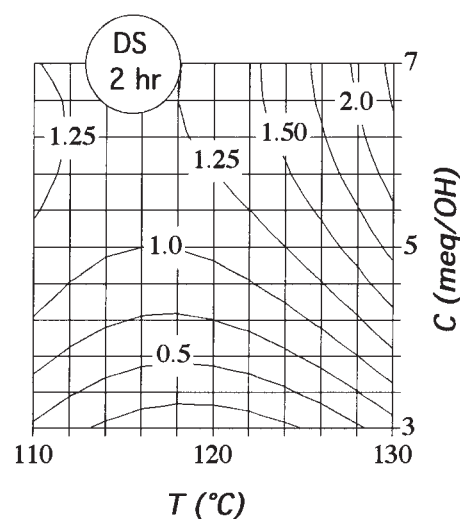


Fig. 5. Isoresponse curves for the total degree of substitution (DS) of the cellulose ester after 2 h of acylation with octanoic acid and acetic anhydride as a function of the temperature ( $T$ ) and the  $H_2SO_4$  catalyst concentration ( $C$ ).

value was obtained at the highest  $T$  and  $C$  values, but the latter were associated with a low RY. The trade-off between the acylation and the formation of oligomers is reflected in the WI values (Fig. 6). The maximum WI was obtained when the lowest temperature was associated with a relatively high catalyst concentration (110°C and 7 meq/OH). Under such conditions, esterification would be predicted to advance without extensive degradation of the cellulosic chain. A new experiment carried out at this point resulted in a medium DS value (1.06) and a RY of 98%, which is in good agreement with the values predicted by the mathematical model derived from the experimental results.

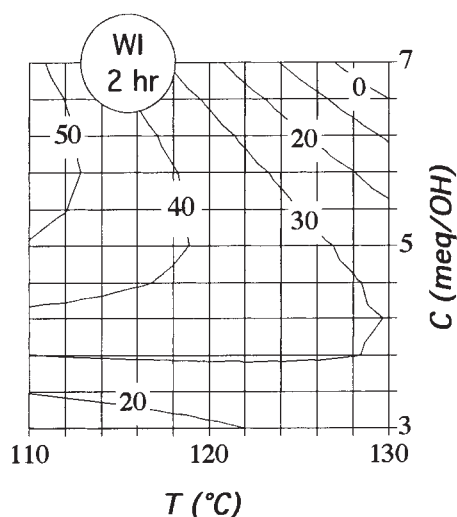


Fig. 6. Isoresponse curves for the weight increase (WI) of the cellulose sample after 2 h of acylation with octanoic acid and acetic anhydride as a function of the temperature ( $T$ ) and the  $\text{H}_2\text{SO}_4$  catalyst concentration ( $C$ ).

### 3.2. Reactions with higher fatty acids

We have tested some linear fatty acids usually derived from plant resources (Table 4) under the conditions predicted to obtain the maximum WI without extensive degradation of the cellulosic chain ( $110^\circ\text{C}$ , 2 h, 7 meq/OH). When the number of carbon atoms ( $n$ ) of the fatty acid increased, the degree of substitution of the fatty acid substituent ( $\text{DS}_n$ ) decreased. This is not surprising since a similar phenomenon was observed in the esterification of wood with fatty acid chlorides (Thiebaud and Borredon, 1995). A longer fatty acid generates a bulkier fatty acylium ion and the steric hindrance is more important. However, the fact that  $\text{DS}_2$  also decreased with increasing  $n$  revealed that the dissociation of the acetic-fatty mixed anhydride was weaker. At a first glance, it could be thought that the mixed anhydride increases its stability when the fatty portion is longer, but in fact, the more disymmetric the anhydride is, the less stable it becomes. Therefore, the diminution of the DS can only be accounted for by the fact that the real concentrations of the catalyst and other reagents decreased. Since the

Table 4  
Effect of the nature of the fatty acid on the mixed acylation of cellulose with acetic anhydride ( $T = 110^\circ\text{C}$ ,  $t = 2$  h,  $C = 7$  meq/OH)

Fatty acid	$n$	$\text{DS}_n$	$\text{DS}_2$	$\text{DS}_{\text{total}}$	WI (%)	RY (%)
Caprylic	8	0.30	0.76	1.06	42	98
Capric	10	0.28	0.75	1.03	44	96
Lauric	12	0.25	0.68	0.93	47	100
Myristic	14	0.22	0.64	0.86	44	98
Palmitic	16	0.19	0.55	0.74	40	95
Stearic	18	0.10	0.31	0.41	25	100

$\text{DS}_n$  = degree of substitution with the fatty acyl group. See Table 2 for abbreviations.

ratio 5.6 eq fatty acid/eq OH was constant for all the experiments, a longer fatty acid represented a larger amount of dispersing agent.

Another phenomenon that could be observed was the progressive increase of the  $\text{DS}_2/\text{DS}_n$  ratio from 2.5 ( $n=8$ ) to 3.1 ( $n=18$ ), which was due to the unequal competition between the small, reactive acetylium ion and the fatty acylium ion, whose molecular weight increases with  $n$ . The acetylation reaction was thus favored when the size of the fatty acid increased.

When passing from  $n=8$  to  $n=12$ , the WI values increased slightly because the molecular weight of the substituent increased while DS values were relatively constant. With longer fatty acids, particularly with stearic acid, the DS values fall so abruptly that WI diminished even if the fatty substituent was heavier. It is also noteworthy that in all cases the RY was higher than 95%, as predicted by the mathematical model derived from the experimental results.

### 3.3. Reactions with lignocellulosic substrates

By eliminating the use of cellulose solvents, it was our purpose to apply the mixed esterification technique to solvent-exchanged LW to modify their surface properties (hydrophobicity). The acylated LW can be interesting for the fabrication of water-repellent particleboards. We wanted to test the reaction conditions that would lead to a high DS with octanoic acid, i.e.,  $T = 130^\circ\text{C}$ ,  $C = 7$  meq/OH,  $t = 2$  h.

The amount of reagents was calculated as if the substrate was cellulose. This operational mode would provide a reagent excess compared to the experiments with cellulose. However, the main components in LW other than cellulose (lignin, hemicelluloses) also contain OH groups that can undergo esterification. The selected LW contained 70–90% holocellulose (cellulose + hemicelluloses) and the number of OH groups per gram of holocellulose is not very different from that in cellulose. Therefore, the differences in yield that may arise from the reagent excess are not substantial.

The evaluation of the esterification yields in LW was achieved by the determination of the ester content by saponification. The total amount of ester functions was thus quantified without differentiation of the acetate from the octanoate groups. The aminolysis technique previously used was avoided in the analysis of LW esters because some non-volatile constituents may dissolve in the pyridine-pyrrolidine mixture and deteriorate the chromatographic column. Proton NMR, which is also a common technique for the analysis of mixed esters (Vaca-Garcia et al., 1998), was not suitable due to the insolubility of the samples and to the interference that other non-cellulosic components may produce in the integration of the signals.



Table 5

Mixed acetic-octanoic acylation of solvent-exchanged and untreated lignocellulosic wastes ( $T = 130^{\circ}\text{C}$ ,  $t = 2$  h,  $C = 7$  meq/OH)

Substrate	Solvent-exchanged		Untreated	
	EC (meq/g)	WI (%)	EC (meq/g)	WI (%)
Cellulose (control)	6700	-24	1440	-5
Pine sawdust	2190	19	1460	15
Wheat straw	2000	3	1190	2
Olive stones	2030	9	1300	7
Agave bagasse	2310	7	1410	4

EC = ester content, WI = weight increase.

All the lignocellulosic residues, pretreated by solvent-exchange, showed comparable reactivities (Table 5, left part). Their EC varied in a narrow range, which was about 3 times lower than that of the cellulose control. However, they presented positive WI values, which revealed that they were less attacked by the acid catalyst. According to Thiebaud (1995), the formation of oligomers by acid degradation is inversely proportional to the lignin content of LW. In our case, this was true for pine, straw and bagasse, as their WI values were larger if their lignin content was high. However, olive stones behaved differently; with a lignin content lower than straw and bagasse, they showed a higher WI. It was concluded that other parameters like porosity and specific volume of the fibers (Rowell et al., 1986), which were not considered in this work, may be useful in explaining this phenomenon.

As an ultimate attempt to further simplify the mixed esterification technique, we eliminated the solvent-exchange pretreatment (Table 5, right part). The comparison of values shows that solvent-exchanged cellulose was four times more esterified than the untreated cellulose and the latter was less degraded during acylation as indicated by its higher WI value. The weaker reactivity of untreated cellulose may have arisen not only from the crystallinity of cellulose, but also from the collapsing of the fiber pores that occurs when commercial cellulose is dried after the pulping process. Therefore, a bulky aliphatic compound (fatty acid or mixed anhydride) cannot penetrate the tight compact structure of the microfibrils. In the solvent-exchange pretreatment, water swells cellulose easily as it interposes between the cellulose chains, reducing intermolecular H-bonding. Next, by washing and stirring with ethanol, the latter replaces water in the interior of the swollen fibers. The fatty acid can be subsequently introduced into the cellulosic microfibrillar structure in the same way. Thanks to the intimate contact between the hydrophilic cellulose fibers and the hydrophobic fatty compounds, the acylation yield of cellulose is increased by about 400%.

In the case of LW, the solvent-exchange technique finds the barrier of lignin and hemicelluloses in the middle lamella surrounding the cellulosic fibers. This results in a positive but limited action of this pretreatment (about 60% increase in acylation). It is worth

noting that untreated cellulose and LW showed almost no difference in acylation yields. This suggests that the collapsing of the fibers during the drying process is the major factor affecting reactivity.

Finally, we tested the hydrophobicity of all the esterified substrates presented in Table 5 by measuring their contact angle with water. All the specimens showed constant values ranging from  $79^{\circ}$  to  $89^{\circ}$ , but no correlation with the ester content could be observed. Such values are, however, significantly superior to the dynamic contact angle of cellulose triacetate ( $70^{\circ}$ ) previously reported (Vaca-Garcia et al., 1998) proving that the grafting of the fatty chains increases the hydrophobicity of the substrates even at low degrees of esterification.

In conclusion, the mixed esterification of cellulose with fatty acids and acetic anhydride was successfully adapted to a solvent-free reaction. Even though the esterification yields were lower than in LiCl/DMAc medium, the products obtained were highly hydrophobic. This technique can be applied to the fatty esterification of lignocellulosic matter. The products thus obtained can be interesting for the production of water-repellent particleboards.

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