# SUBPRODUCTOS EN LA FABRICACIÓN DE PASTAS. AUTOHIDRÓLISIS DE LAS HEMICELULOSAS

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## 20.1. INTRODUCCIÓN

La necesidad de utilizar la fracción de celulosa de la biomasa vegetal para producir pastas celulósicas implica una pérdida potencial de otros componentes estructurales presentes en los materiales lignocelulósicos (1,2). Esto sugiere la conveniencia de integrar líneas de producción de subproductos en la fabricación de pasta celulósica, al objeto de aprovechar las fracciones constituidas por hemicelulosas y lignina.

Diferentes procesos que se enmarcan dentro del concepto del aprovechamiento fraccionado de los materiales lignicelulósicos han sido considerados en la bibliografía (3), fundamentalmente para maderas de coníferas y frondosas.

Sin embargo, en el caso de los materiales residuales como los procedentes de las actividades agrícolas y agroindustriales, el fraccionamiento adquiere especial interés por cuanto supondría un beneficio ecológico al eliminar la fuente de contaminación, al tiempo que los dotaría de un valor añadido que no tienen como tales residuos.

El fraccionamiento de materiales lignocelulósicos también es interesante aplicarlo a otros materiales alternativos a las maderas convencionales para la fabricación de pastas celulósicas (frondosas y coníferas) como son ciertos vegetales anuales y algunos vegetales de interés industrial de crecimiento rápido (sorgo papelero, kenaf, tagasaste, paulownia, etc.). En lo sucesivo se considera como materiales alternativos, tanto a los aquí señalados como a los residuos agrícolas y de industrias agroindustriales.

Una de las posibles opciones de fraccionamiento consiste en someter los materiales alternativos a una etapa previa de autohidrólisis para la despolimerización de las hemicelulosas. De ella resulta una fracción acuosa que contiene azúcares hemicelulósicos formados por xilo-oligosacáridos y monosacáridos (xilosa, glucosa, arabinosa, etc.), y un resto sólido no solubilizado constituido mayoritariamente por celulosa, que reúne condiciones muy favorables para su transformación en pasta celulósica.

En este sentido, el desarrollo del capítulo atiende a la presentación de los conceptos generales relativos a la autohidrólisis de las hemicelulosas, obviándose los concernientes a los procesos de hidrólisis ácida y enzimática de las hemicelulosas y al de pasteado, por haber sido tratados anteriormente. Asimismo se considera su aplicación práctica para tallos de girasol, al objeto de evaluar las posibilidades de obtención de azúcares por autohidrólisis y su adecuación al proceso de pasteado organosolv con etanol-agua. Los resultados del procedimiento ensayado insinúan logros de interés, no sólo desde el punto de vista de viabilidad técnica para la obtención de los productos considerados, sino como vía de valorización y de solución medioambiental de este residuo agrícola.

## 20.2. COMPOSICIÓN DE LAS HEMICELULOSAS

En los materiales lignocelulósicos se distinguen los componentes estructurales de la pared celular (celulosa, hemicelulosa y lignina), que representan el 80-90% del peso total, y los componentes no estructurales (agua, sustancias extraíbles, cenizas y otros).

Las hemicelulosas, término utilizado para aludir a los polisacáridos de la pared celular extraíbles con álcalis acuosos, incluyen a todos los polisacáridos estructurales salvo la celulosa (4,5). Su función en la pared celular es servir de puente de unión entre la celulosa y la lignina. Estas se encuentran en proporciones del 20 al 30%, variando mucho de un material a otro, siendo mayor en los materiales alternativos que en los materiales madereros que presentan mayores contenidos en celulosa y lignina. Las hemicelulosas se diferencian de la celulosa por su mayor velocidad de hidrólisis en medio ácido y por su solubilidad en álcalis, y en cuanto a la lignina por su resistencia a la oxidación.

Bajo la denominación hemicelulosas se encuentra un grupo de heteropolímeros constituidos por un pequeño número de azúcares y algunos de sus derivados, como azúcares acetilados y ácidos urónicos. Las hemicelulosas están constituidas principalmente por tres hexosas (glucosa, galactosa y manosa) y dos pentosas (xilosa y arabinosa). También pueden aparecen en pequeñas cantidades ramnosa y fucosa (4).

Otras diferencias que presentan las hemicelulosas con respecto a la celulosa son el grado de polimerización (entre 200-300 en las hemicelulosas frente a 500-15.000 de la celulosa); la presencia de ramificaciones (la celulosa es un polímero lineal, sin ninguna ramificación); la heterogeneidad (las hemicelulosas son heteropolímeros formados por distintos azúcares que pueden presentar sustituyentes, mientras que la celulosa es un homopolímero que está compuesto únicamente por glucosa); y la falta de cristalinidad (presenta una estructura amorfa, a diferencia de la celulosa que posee una acusada cristalinidad).

En la Tabla 20-1 se muestra la composición de las hemicelulosas presentes en diversos materiales (1,6-12). Dicha composición se expresa en función de los monómeros constituyentes de las hemicelulosas, cuantificados por cromatografía líquida de alta resolución.

Los datos bibliográficos señalan que la xilosa es el monómero mayoritario en las maderas de frondosas y en los materiales alternativos, mientras que la manosa aparece en cantidades importantes en las maderas de coníferas. Los grupos acetilo son más abundantes en las maderas de frondosas (3,8%) que en las de coníferas (1,4%), presentando los materiales alternativos un contenido intermedio (3,3%).

La denominación habitual que reciben los diferentes heteropolímeros que forman las hemicelulosas se deriva del monómero mayoritario. A continuación se describen los principales heteropolímeros hemicelulósicos (4,13-20).

### 20.2.1. Xilanos

Después de la celulosa, los xilanos son los polisacáridos más abundante en los vegetales. Los xilanos son los heteropolímeros mayoritarios en las maderas de frondosas y en los materiales alternativos, mientras que en las maderas de coníferas su presencia es menor, aunque en porcentajes apreciables. En las maderas de coníferas aparece como arabinoglucoroxilano, formado por un esqueleto de xilosa con ramificaciones laterales de ácido metilglucourónico (4-o-acetil-metil-o-glucourónico) o arabinofuranosa, que estabilizan la molécula frente a las bases. Su grado de polimerización es aproximadamente 100. En cuanto a las maderas de frondosas, las ramificaciones del esqueleto están formadas por ácido metilglucourónico o por grupos acetilo, con trazas de arabinosa. Este es un polímero más largo, con un grado de polimerización de aproximadamente 190 unidades. El enlace del ácido metilglucourónico es mucho más resistente a la acción de los ácidos que los enlaces de la xilosa o de los grupos acetilo, que se degradan más fácilmente.

En los materiales alternativos se encuentra diversidad de xilanos, normalmente más parecidos a los de las maderas frondosas pero con más arabinosa. Así, el esparto presenta un homopolímero compuesto únicamente por unidades de xilosa con enlaces $\beta,1\rightarrow 4$ y un grado de polimerización pequeño, en torno a 65 unidades. Otros materiales, como bambú, paja de cebada o canela presentan heteropolímeros similares a los de las maderas de frondosas, con grados de polimerización entre 90 y 130 y una distribución de azúcares diferente, destacando la mayor cantidad de arabinosa. En el salvado de trigo el 65% de las unidades de xilosa presentan ramificaciones de arabinosa, mientras que en la paja de trigo sólo el 7,7% las presentan (21). En el maíz existen xilanos compuestos por un esqueleto de unidades de xilosa con enlaces $\beta 1\rightarrow 4$ con diversos sustituyentes y bastantes ramificaciones donde se encuentran xilosa y galactosa.

### 20.2.2. Mananos

Los mananos representan el grupo de heteropolímeros predominantes en las maderas de coníferas, apareciendo en pequeñas proporciones en maderas de frondosas y en los materiales alternativos. En las maderas de frondosas aparecen cadenas formadas por manosa y glucosa, sin ramificaciones, mientras que en maderas de coníferas y materiales alternativos se observa el mismo esqueleto pero con ramificaciones de una galactosa, muy susceptibles a la hidrólisis por ácidos. En estos dos últimos materiales, al aumentar el número de unidades de galactosa aumenta la solubilidad en agua y disminuye la solubilidad en álcalis.

### 20.2.3. Galactanos

Los galactanos están presentes en los materiales lignocelulosicos en menor proporción que los xilanos y mananos, y son muy solubles en agua. En las maderas de coníferas estos heteropolímeros presentan una estructura muy ramificada con residuos laterales de arabinosa y/o ácidos urónicos o cadenas de varias unidades que comienzan por galactosa. Aparecen también en las maderas de frondosas, con ramnosa en las ramificaciones, pudiendo encontrarse en menores proporciones xilosa, ácido glucourónico y ácido galactourónico.

### 20.2.4. Glucanos

Los glucanos son compuestos constituidos mayoritariamente por unidades de glucosa. El heteropolímero laricina está presente en las maderas de coníferas y algunos materiales alternativos en porcentajes del 2-4%, con un grado de polimerización de 170-205, ramificado y con enlaces $\beta1\rightarrow3$. La laricina presenta trazas de ácidos glucourónico y galacturónico.

### 20.2.5. Xiloglucanos

Los xiloglucanos se encuentran en pequeñas proporciones en las maderas de coníferas. Es un heteropolímero de glucosa y xilosa que puede presentar trazas de arabinosa, galactosa, fucosa, ramnosa y grupos acetilo. Probablemente desempeñen su función durante el crecimiento del vegetal.

### 20.2.6. Sustancias pécticas

Estas sustancias constituyen un conjunto de heteropolímeros caracterizado por un esqueleto formado por unidades del ácido galactourónico. Se encuentran en la pared primaria y sobre todo en la laminilla media. Son más abundantes cuando la célula es joven. En las maderas están presentes en porcentajes menores del 1% y pueden presentar monómeros de ramnosa formando parte del esqueleto. Debido a su estructura, tienen la propiedad de formar geles de alta viscosidad en disoluciones acuosas, pudiendo ser utilizados como espesantes.

## 20.3. DESPOLIMERIZACIÓN DE LAS HEMICELULOSAS POR AUTOHIDRÓLISIS

La bibliografía es extensa en la descripción de procesos para el aprovechamiento de los materiales lignocelulósicos. Algunos de estos procesos consiguen la valorización de los materiales lignocelulósicos en un solo paso (aprovechamiento global o integral), mediante las operaciones de combustión (22,23), gasificación (24), pirólisis (25) y licuefacción (26,27), con fines energéticos principalmente. Otros procesos consisten en un fraccionamiento selectivo de los principales componentes de la biomasa (aprovechamiento fraccionado), como son los métodos de deslignificación, de hidrólisis de polisacáridos y los mixtos, para la recuperación individualizada de todos o alguno de ellos; la principal dificultad de esta estrategia está en la imposibilidad de separar de forma diferenciada la celulosa, hemicelulosas y lignina sin degradar sus estructuras químicas (28).

Los procedimientos concernientes a la deslignificación han sido expuestos con anterioridad en los diferentes procesos de pasteado. De igual manera, también se han presentado los procesos de hidrólisis ácida y enzimática de los polisacáridos para su transformación en sus azúcares constituyentes.

Otra opción para la despolimerización de las hemicelulosas es la autohidrólisis, también conocido como proceso hidrotérmico, que no requiere la adición de ácidos al autogenerarse en el propio medio. Sus aspectos más relevantes se tratan a continuación.

### 20.3.1. Fundamento de la autohidrólisis

Existen varios tipos de procesos hidrotérmicos, todos ellos basados en la autohidrólisis y que comparten el mismo fundamento químico, pero que presentan diferencias en el modo de operación. Además del propiamente conocido como de autohidrólisis, es muy significativo el proceso de explosión con vapor (una vez transcurrida la autohidrólisis, la mezcla se somete a una descompresión súbita para provocar la vaporización del agua contenida en las fibras y la consiguiente desagregación de la matriz lignocelulósica) y sus variantes, tales como los procesos RASH (29), Masonite (30,31), IOTECH (3,32), Siropulper (31,33) y STAKE (34,35,36).

La autohidrólisis de las hemicelulosas consiste en tratar los materiales lignocelulósicos en medio acuoso a temperaturas entre 150-250 ºC. Bajo estas condiciones, la autoionización del agua genera protones que actúan como catalizador de la hidrólisis de las hemicelulosas, atacando entre otros a los grupos acetilo (presentes en forma de ésteres en los heteropolímeros hemicelulósicos), que se liberan en forma de ácido acético. La contribución de éste a la generación de protones es de 1.700 a 1.000.000 veces mayor que la del agua, por lo que puede despreciarse la contribución de los protones acuosos al proceso hidrotérmico una vez se ha generado ácido acético (37,38). Al mismo tiempo se produce la solubilización total o parcial de las hemicelulosas y su conversión con buenos rendimientos de oligosacáridos y monosacáridos, que pueden utilizarse para distintos propósitos (39,40-43).

Otras reacciones de menor importancia que aparecen asociadas a este tipo de procesos son la formación de productos como el furfural a partir de las pentosas y del 5-hidroximetil-2-furfural (HMF) a partir de las hexosas (46); la generación de anhídrido carbónico por descomposición de los grupos carboxilo presentes en los ácidos urónicos (45); la condensación de algunas moléculas inestables que intervienen como intermedios de reacción; la descomposición en condiciones severas de productos como el furfural, sensibles a la concentración de ácido (44); la descomposición del HMF a ácidos fórmico y levulínico; y las reacciones de condensación con la lignina (40,47).

Respecto de la hidrólisis ácida, la autohidrólisis presenta las siguientes ventajas: mayor simplicidad de la estructura del proceso, menor impacto ambiental por la ausencia de lodos resultantes de la neutralización del ácido, y la posibilidad de someter la suspensión resultante a una descompresión súbita (explosión con vapor) para causar la desagregación de la matriz lignocelulósica (34,48) que resulta favorable para un posterior procesamiento a efectos de obtención de pastas celulósicas.

### 20.3.2. Condiciones de operación en la autohidrólisis de las hemicelulosas

Los tratamientos hidrotérmicos pueden llevarse a cabo en un intervalo de condiciones de operación muy amplio. Las variables más influyentes en este tipo de tratamientos son la temperatura, tiempo, concentración de sólidos y tamaño de partícula.

#### 20.3.2.1. Temperatura

Suele fijarse como límite inferior de referencia una temperatura de 100 ºC (49), dado que por debajo de esta temperatura no se producen procesos de autohidrólisis (50). En cuanto al límite superior se ha operado a temperaturas de hasta 300 ºC (51). Atendiendo a criterios de selectividad del proceso para favorecer las reacciones de polimerización de las hemicelulosas es preciso establecer el rango de operación de temperaturas que convenga. Así, para un proceso hidrotérmico en medio ácido débil se advierte que los enlaces éter de la lignina comienzan a romperse a 160-180 ºC (34), mientras que las reacciones de despolimerización de la celulosa se inician a temperaturas superiores a 210 ºC (37).

#### 20.3.2.2. Tiempo de operación

El tiempo de operación puede variar desde segundos hasta varias horas. En tratamientos a temperaturas relativamente elevadas suele ser importante el tiempo de calentamiento (rampa de calentamiento) necesario para alcanzar la temperatura fijada de operación (52). En algunos casos, el tiempo de calentamiento puede ser muy superior al de operación o reacción, mientras que el tiempo de enfriamiento suele ser comparativamente pequeño (velocidad de enfriamiento de 30 ºC/min) y no influye apreciablemente en el proceso (53,54).

#### 20.3.2.3. Concentración de sólidos

La concentración de sólidos se expresa habitualmente mediante la relación “líquido/sólido” (RLS), parámetro que relaciona la cantidad de agua que se añade por unidad de masa de sólido (sobre base libre de humedad). En la bibliografía se encuentran valores entre 2 y 40 g de agua/g de material lignocelulósico, aunque lo habitual es alrededor de 10 g/g. Un valor elevado de la RLS beneficia la extracción de las hemicelulosas pero es muy costoso, mientras que valores bajos son económicamente más favorables en principio, aunque pueden provocar problemas de limitaciones difusionales y de transporte de los productos de reacción.

#### 20.3.2.4. Tamaño de partícula

Un tamaño de partícula pequeño facilita el tratamiento hidrotérmico, pero aumenta considerablemente el gasto energético en la molienda. Alternativamente, un tamaño grande puede dar lugar a limitaciones difusionales. Lo usual en los trabajos de laboratorio son tamaños de partícula en el intervalo 0,5-10 mm, mientras que a escala industrial o de planta piloto son normales tamaños de varios centímetros. El estudio de la influencia del tamaño de partícula sobre el proceso ha sido considerado por algunos autores (55,56).

Si se tiene en cuenta que en condiciones severas las hemicelulosas se solubilizan en gran proporción, pero también aumenta significativamente los productos de descomposición no deseados (furfural y HMF), es preciso encontrar un conjunto de valores de operación que da lugar a un máximo de hemicelulosas solubles recuperables en la fase líquida como azúcares individuales o como oligómeros (productos deseados), compatibles con la minimización de formación de productos de degradación (57-60).

### 20.3.3. Efectos de los tratamientos hidrotérmicos sobre las hemicelulosas

Durante los tratamientos hidrotérmicos el ácido acético crea un medio ácido con valores de pH comprendidos entre 3 y 4 (50,59,61,62), en el cual se despolimerizan las hemicelulosas, generándose una mezcla de oligómeros de azúcares, monosacáridos y, dependiendo de las condiciones de operación, productos de descomposición de éstos. En condiciones adecuadas la suma de oligosacáridos y monósacáridos (xilosa, glucosa, arabinosa, etc.) procedentes de las hemicelulosas oscila entre el 60 y el 85% del total de las hemicelulosas iniciales (40,57,58,60,63). La proporción de oligosacáridos que aparecen en los licores hidrotérmicos es superior a la de monosacáridos, pudiendo representar más de la mitad de las hemicelulosas iniciales (40,41,51,57,58,64,65).

La explicación de que la recuperación de oligómeros de azúcares y monosacáridos en la fase líquida no sea cuantitativa respecto de la fracción solubilizada se debe a la participación de reacciones de degradación, que conducen a furfural y HMF muy sensibles a las condiciones de operación seleccionadas, pudiéndose encontrar porcentajes muy variados de estos para un mismo material (47,50,58,59,63).

Los tratamientos hidrotérmicos en condiciones relativamente suaves de operación no provocan alteraciones de consideración sobre la celulosa, para lo que se necesita alcanzar temperaturas superiores a 260 ºC (66). En cuanto a la lignina, parte de ella se solubiliza a consecuencia de la rotura de los enlaces éter.

Este comportamiento de los procesos hidrotérmicos, en el que se obtienen residuos sólidos susceptibles a la deslignificación, le otorga a los materiales lignocelulósicos la posibilidad de obtener pasta celulósica, configurándose así la vía de aprovechamiento que integra la recuperación de subproductos azúcares en la producción de pasta (67-72).

## 20.4. UTILIZACIÓN COMERCIAL DE LOS PRODUCTOS DE LA DESPOLIMERIZACIÓN DE LAS HEMICELULOSAS

### 20.4.1. Aplicaciones de los azúcares hemicelulósicos como medios de cultivo en procesos fermentativos

La autohidrólisis consigue la solubilización de las hemicelulosas a oligosacáridos y monosacáridos con rendimientos entre el 55-99% (73). Una interesante aplicación de estos licores es la vía fermentativa para obtener compuestos como el etanol o el xilitol. Dado que los microorganismos productores de estas sustancias no metabolizan los oligómeros, resulta necesario tras la autohidrólis un segundo tratamiento químico para provocar la ruptura de los oligómeros a sus monómeros constituyentes (principalmente xilosa, además de glucosa y arabinosa), denominado posthidrólisis (hidrólisis con ácido sulfúrico a bajas concentraciones a 120 ºC y tiempos de hasta 1 hora). De esta manera, la conjunción de los procesos de autohidrólisis y posthidrólisis conducen a una mezcla de monómeros de azúcares aptos para el medio de cultivo en procesos fermentativos.

### 20.4.2. Aplicaciones de los xilo-oligosacáridos

El licor resultante de la autohidrólisis de los materiales lignocelulósicos está principalmente constituido por xilo-oligosacáridos. Tras un proceso de separación y purificación pueden ser utilizados en diversos campos:

- Agricultura: como estimulantes y aceleradores del crecimiento.
- Alimentación animal: para animales domésticos y peces.
- Farmacia: para prevención y tratamiento de enfermedades gastrointestinales, tratamiento de dolencias como osteoporosis, otitis y problemas del cabello y la piel.
- Alimentación humana: ingredientes de alimentos reforzados, alimentos especiales (dietas antiobesidad) o alimentos simbióticos (que contienen microorganismos además de principios alimentarios con efectos positivos sobre la salud).

En referencia a su aplicación como ingredientes de alimentos, los xilo-oligosacáridos presentan un buen aroma y son bajos en calorías, lo que favorece su utilización en dietas de adelgazamiento (74). Además, los efectos de los xilo-oligosacáridos sobre la salud están relacionados principalmente con su acción sobre la flora gastrointestinal, al ser una fuente de carbono para las bacterias intestinales beneficiosas (bifidobacterias), promoviendo su crecimiento (75,76) y aportando efectos benéficos en la salud humana: limitan la actividad de las bacterias entero-putrefactas (77), evitan la proliferación de bacterias patógenas (76) y favorecen la digestión y absorción de nutrientes. Estas propiedades permiten que los oligosacáridos cumplan los requisitos exigidos para los componentes prebióticos de los alimentos y sean utilizados como ingredientes activos de los alimentos funcionales.

## 20.5. PROCESO INTEGRAL DE AUTOHIDRÓLISIS Y PASTEADO, CON ETANOL, DE TALLOS DE GIRASOL

En España se recolecta anualmente 1.300.000 t de girasol, de los que aproximadamente una tercera parte corresponden a Andalucía (78). Esta actividad genera una cantidad importante de residuos que deben ser tratados para minimizar su negativo impacto ecológico. La mejor solución medioambiental para los tallos de girasol implica adoptar estrategias de valorización que permitan su eliminación como fuente de contaminación y la consecución de un beneficio económico por aprovechamiento de sus componentes estructurales.

En relación con lo anterior, se ensaya un proceso para la obtención conjunta de azúcares hemicelulósicos y de pasta de celulosa, mediante un pretratamiento hidrotérmico del material, para provocar la autohidrólisis de las hemicelulosas, y un posterior pasteado del residuo sólido resultante con una mezcla de etanol-agua.

### 20.5.1. Autohidrólisis de las hemicelulosas de tallos de girasol

El material, previo secado y trituración hasta un tamaño de entre 10 y 20 mm, se introduce en un reactor de alta presión, provisto de sistemas de calefacción, agitación y control de temperatura. El hidromódulo empleado es de 8 g agua/g materia prima. La suspensión se calienta siguiendo el perfil de calentamiento estándar del reactor hasta alcanzar la temperatura fijada de operación.

Para evaluar la influencia del tratamiento hidrotérmico de autohidrólisis sobre el grado de fraccionamiento de la materia prima, se realizan distintas experiencias en condiciones no isotermas, para el intervalo de temperaturas de 160 a 200 ºC. Dicho intervalo se justifica tomando como referencia las indicaciones bibliográficas, siendo previsible bajos rendimientos de autohidrólisis a bajas temperaturas, mientras que por encima de 210 ºC la despolimerización de la celulosa suele ser muy importante. Una vez alcanzada la temperatura de operación, se mantiene durante unos segundos para evitar en lo posible la aparición de productos de descomposición y degradación de la celulosa. Finalmente, la suspensión se enfrió gradualmente hasta temperatura ambiente.

En la tabla 20-2 se indica el porcentaje del material solubilizado en función de la temperatura de operación en el proceso hidrotérmico. La influencia de la temperatura en la autohidrólisis de las hemicelulosas es determinante sobre el porcentaje de la fracción solubilizada, presentando ésta un máximo de 26,1% para 190 ºC.

La concentración en la fase líquida de los diferentes azúcares y otros componentes resultantes de la hidrólisis de las hemicelulosas, analizados por cromatografía líquida de alta resolución, se muestran en la tabla 20-3. Se observa que la cantidad total de azúcares experimenta un aumento progresivo en la fase líquida conforme se incrementa la temperatura de operación, detectándose un máximo de 26,9 g/l de xilo-oligosacáridos y 4,2 g/l de monómeros (glucosa, xilosa y arabinosa) para la temperatura de 190 ºC. En cuanto al contenido relativo de los diferentes azúcares los xilo-oligosacáridos son mayoritarios, siendo poco significativa la presencia de los monómeros. También se advierte la aparición de ácido acético (resultante del ataque de los protones a los grupos acetilo) y otros productos de degradación por reacciones secundarias asociadas a la hidrólisis. Esta presencia inevitable está en sintonía con trabajos similares (63,41).

En la tabla 20-4 se muestran los rendimientos de producción de azúcares hemicelulósicos mediante el tratamiento hidrotérmico. Los resultados constatan la alta eficiencia de la autohidrólisis de los tallos de girasol para la obtención de xilo-oligosacáridos, cuando se opera a temperaturas superiores de 180 ºC. El máximo encontrado es de 21,5 g de xilo-oligosacáridos / 100 g de materia prima, a la temperatura de 190 ºC.

### 20.5.2. Pasteado con etanol del residuo sólido del tratamiento hidrotérmico de los tallos de girasol

Sobre el residuo sólido del pretratamiento hidrotérmico se lleva a cabo un estudio de deslignificación mediante el proceso organosolv que utiliza etanol-agua, con el objeto de su aprovechamiento para la obtención de pasta celulósica.

A efectos de conjunción de intereses que compatibilicen adecuados rendimientos de extracción de azucares con una aceptable calidad de las pastas celulósicas a partir del sólido resultante de la autohidrólisis, es preciso encontrar una solución de compromiso para la temperatura de operación durante esta operación. Así, si el tratamiento hidrotérmico se lleva a cabo en condiciones severas la recuperación de azúcares es muy eficiente, sin embargo es inevitable un incremento de la degradación de la fibra celulósica del material con efecto adverso sobre la calidad de la pasta celulósica (pastas de baja viscosidad).

En base a la argumentación anterior, se estima oportuno fijar la temperatura del pretratamiento hidrotérmico en 180 ºC, ligeramente inferior a la encontrada como óptima, a fin de compatibilizar ambos propósitos; es decir, preservar la ruptura de la estructura de la celulosa para la obtención de pasta celulósica y conseguir fracciones solubilizadas con aceptables contenidos de azúcares.

Muestras de la fase sólida resultante del proceso de autohidrólisis a temperatura de 180 ºC, son sometidas al proceso de pasteado con etanol-agua en el mismo reactor de autohidrólisis, fijando un hidromódulo de 8 g disolución/ g residuo sólido. Las variables de operación y los intervalos ensayados son: temperatura de 145 a175 ºC, concentración de etanol de 40 a 70 % y tiempo de pasteado de 40 a 120 minutos. La selección de los experimentos se ajustó a un diseño por cuadrados latinos a cuatro niveles. Las pastas separadas por filtración se lavan y se someten a operaciones de desintegrado (1200 rpm durante 20 minutos), desfibrado (en refinador Sprout-Waldron) y separado de incocidos (filtro Strainer de 0,4 mm de luz) .

En la tabla 20-5 se especifican las condiciones de operación del pasteado y las características químicas de las pastas celulósicas resultantes, determinadas por la metodología estándar. Los datos revelan rendimientos que varían entre 41,16 y 65,58% (valor medio 51,46%) y contenidos en α-celulosa entre 41,9 y 56,7% (valor medio 47,64%), que pueden considerarse aceptables desde el punto de vista de la producción de pasta para papel.

Para comprobar la bondad del procedimiento de autohidrólisis-pasteado sobre la calidad de las hojas de papel obtenidas a partir de las pastas producidas, una vez refinadas éstas se proceda a la formación de hojas y a su caracterización física, cuyos resultados se muestran en la tabla 20-6. A partir de estos datos se realiza un análisis comparativo con trabajos similares.

Garrote y col. (79), por aplicación del mismo procedimiento a madera de eucalipto obtuvieron valores máximos de longitud de rotura de 3,2 km, índice de estallido de 0,87 kPa·m$^2$/g e índice de desgarro de 1,11 kN·m$^2$/g, valores ligeramente inferiores a los obtenidos para tallos de girasol, cuyos máximos son de 3,85 km, 1,58 kPa·m$^2$/g y 2,73 kN·m$^2$/g, respectivamente. Jiménez y col. (80) aplicaron un proceso de pasteado con etanol-agua a la paja de trigo sin pretratamiento hidrotérmico, resultando hojas de papel de características físicas del mismo orden a las obtenidos en este trabajo. Khristova y col. (81), mediante pasteado de tallos de girasol con sosa-antraquinona, sin tratamiento previo de autohidrólisis de las hemicelulosas, obtuvieron hojas de papel con mejores características físicas; sin embargo, este tratamiento de pasteado tradicional respecto de los organosolv es medioambientalmente menos ventajoso.

En definitiva, se constata la viabilidad técnica y los eficientes resultados del procedimiento ensayado como alternativa de solución medioambiental para los tallos de girasol y su consiguiente valorización, al ser un material residual apto para la producción conjunta de oligosacáridos y de pasta para papel.

Completada la anterior fase de estudio se procede a la concreción de los valores óptimos de operación en el proceso de pasteado, asumiendo como temperatura idónea la de 180 ºC para el pretratamiento hidrotérmico. Para ello, se ajustan los datos de las tablas 20-4 y 20-5 a modelos matemáticos (polinómicos de segundo grado) que determinan la influencia de las variables independientes o de operación (temperatura, tiempo y concentración de etanol) sobre las variables dependientes o características de las pastas (rendimiento, α-celulosa, índice kappa, viscosidad, grado de refino, longitud de rotura e índice de estallido).

En la tabla 20-7 se presentan las ecuaciones encontradas para las distintas variables dependientes consideradas. Estas ecuaciones, con coeficientes $r^2$ entre 0,82 y 0,97, estiman los valores de todas las variables dependientes con un errores menores del 10%.

A partir de las ecuaciones anteriores y mediante la visualización de gráficas en las que se representan las superficies de respuesta de cada variable dependiente frente a las variables independientes o de operación, para niveles máximo y mínimo de la variable independiente más influyente, es posible realizar un análisis del comportamiento global del proceso de pasteado y extraer conclusiones acerca de las condiciones optimas de operación. A guisa de ejemplo, en la figura 20-1 se representa el rendimiento en función del tiempo y de la concentración de etanol, para valores elevado y bajo de la temperatura.

Las mejores propiedades químicas de las pastas se obtienen a temperaturas, tiempos y concentraciones de etanol altas. En cuanto a las propiedades físicas de las hojas de papel, se ven favorecidas con aumentos de la temperatura, aunque para tiempos y concentraciones altas dichas propiedades decaen significativamente. Considerando que son deseables máximos valores de las propiedades químicas de las pastas y físicas de las hojas de papel correspondientes, es preciso adoptar un conjunto de valores de las variables de operación que compatibilice tal propósito. En consecuencia, es preciso operar en la etapa de pasteado a temperaturas altas (175 ºC), tiempos medio-bajos (60 minutos) y concentraciones de etanol moderadamente bajas (50 %).

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Tabla 20-1.- Composición de las hemicelulosas en los materiales lignocelulósicos (% en peso referido al material seco)

| Material lignocelulósico | Xilosa | Manosa | Galactosa | Arabinosa | Grupos acetilo | Ácidos urónicos[1] |
|---|---|---|---|---|---|---|
| MADERAS DE CONÍFERAS | | | | | | |
| Pícea glauca | 6,8-9,1 | 11-12 | 1,2-1,9 | 1,1-1,6 | 1,2-1,3 | 3,6-4,4 |
| Pícea mariana | 6 | 9,4 | 2 | 1,5 | 1,3 | 5,1 |
| Pícea rubens | 6,2 | 12 | 2,2 | 1,4 | 1,4 | 1,7 |
| Pseudotsuga | 2,8 | 11 | 4,7 | 2,7 | 0,8 | 2,8 |
| Pícea abies | 5,6-7,6 | 9,5-13,6 | 2,3-2,8 | 0,5-1,4 | 1,2-2,5 | 1,4-5,3 |
| Larix decidua | 5,1-6,3 | 11-11,5 | 2-6,1 | 2-2,5 | 1,4 | 2,2-4,8 |
| Pinus radiata | 6,2-6,5 | 9,5-12 | 2,8-3,3 | 2,1-2,7 | 1,9-2 | 2,5-5,1 |
| Pinus resinosa | 7,9-9,3 | 7,4-10,7 | 1,8-2 | 2-2,4 | 1,2 | 6 |
| Pinus rigida | 6,6 | 9,8 | 1,4 | 1,3 | 1,2 | 1,4 |
| Pinus sylvestris | 7,6 | 10-12,4 | 1,9-3,1 | 1,5-1,6 | 1,3 | 5-5,6 |
| Pinus taeda | 6,5-6,8 | 10,5-11 | 2,3-2,4 | 1,5-1,7 | 1,1 | 3,8 |
| MADERAS DE FRONDOSAS | | | | | | |
| Abedul | 20-26 | 1,8-3,6 | 0,6-1,3 | 0,3-0,6 | 3,3-4,4 | 4,2-6,3 |
| Álamo | 15,2-21,2 | 2,1-3,5 | 0,8-2 | 0,4-0,9 | 3,2-3,9 | 3,1-5,2 |
| Arce | 15-19 | 2,3-3,3 | 0,6-1 | 0,5-1 | 2,9-3,8 | 3,5-4,4 |
| Eucalyptus globulus | 21,5 | 0,7 | 2,5 | 1,8 | 7,3 | 1,8 |
| Fagus sylvatica | 19-21,7 | 0,9-2,1 | 0,8-1,4 | 0,5-0,9 | 3,9-4,3 | 4,8-5,9 |
| Ulmus | 12-15,1 | 2,4-3,4 | 0,9 | 0,4-0,6 | 3-3,9 | 4,6-4,7 |
| Quercus falcata | 19-21,7 | 2-2,4 | 1,2-2,1 | 0,4-1,6 | 3,3 | 4,5 |
| MATERIALES ALTERNATIVOS | | | | | | |
| Bagazo caña | 21,5 | 0 | 0 | 2,7 | - | - |
| Cascarilla arroz | 12,3 | 2,7 | 0,1 | 2,6 | - | - |
| Paja de cebada | 15 | 1,3 | 1,7 | 4,0 | - | - |
| Tallos de maíz | 13-21,1 | 0-0,25 | 0,7-0,8 | 2,8-3,7 | 3,6 | 4,4 |
| Zuros de maíz | 29,1 | 0 | 0 | 2,8 | - | - |
| Paja de arroz | 13 | 1,6 | 0,4 | 4,0 | - | - |
| Paja de sorgo | 15,0 | 0,8 | 0,2 | 3,0 | - | - |
| Paja de trigo | 16,9-18,5 | 0-0,7 | 0,7-2,2 | 1,6-2,1 | 2,4 | 2,2 |

[1]: Incluye ácidos glucourónico, metilglucourónico y galactourónico.

Tabla 20-2. Fracciones solubilizadas en el tratamiento hidrotérmico de los tallos de girasol (porcentajes referidos a la cantidad de materia prima)

| Temperatura (ºC) | (∗) Fracción no solubilizada (%) | Fracción solubilizada (%) |
|---|---|---|
| 1 | 85,7 | 14,0 |
| 165 | 84,1 | 15,2 |
| 170 | 81,1 | 18,7 |
| 175 | 80,3 | 19,5 |
| 180 | 78,4 | 20,9 |
| 190 | 73,7 | 26,1 |
| 200 | 72,5 | 24,5 |

(∗) Representa el rendimiento respecto de la materia prima en términos de su utilización para un proceso de pasteado

Tabla 20-3. Concentración de componentes extraídos de la fracción hemicelulósica de tallos de girasol en el tratamiento hidrotérmico

| Temperatura (ºC) | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|
| Oligosacáridos (g/L) | 9,5 | 11,3 | 13,6 | 21,0 | 24,2 | 26,9 | 23,3 |
| Glucosa (g/L) | 0,5 | 0,6 | 1,2 | 0,8 | 1,2 | 1,0 | 0,7 |
| Xilosa (g/L) | 1,3 | 1,6 | 1,7 | 2,0 | 1,9 | 2,6 | 2,1 |
| Arabinosa (g/L) | 0,0 | 0,1 | 0,2 | 0,3 | 0,5 | 0,6 | 0,6 |
| Acido fórmico (g/L) | 0,2 | 0,3 | 0,3 | 0,4 | 0,8 | 0,8 | 1,0 |
| Acido acético (g/L) | 0,4 | 0,5 | 1,0 | 1,1 | 2,4 | 2,4 | 4,6 |
| HMF(g/L) | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 |
| Furfural (g/L) | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 |

Tabla 20-4. Recuperación de azúcares hemicelulósicos de tallos de girasol por tratamiento hidrotérmico (g azúcar / 100 g material)

| Temperatura (ºC) | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|
| Oligosacáridos | 7,60 | 9,03 | 10,87 | 16,79 | 19,35 | 21,51 | 18,63 |
| Glucosa | 0,40 | 0,48 | 0,96 | 0,64 | 0,96 | 0,80 | 0,56 |
| Xilosa | 1,04 | 1,28 | 1,36 | 1,60 | 1,52 | 2,08 | 1,68 |
| Arabinosa | 0,00 | 0,08 | 0,16 | 0,24 | 0,40 | 0,48 | 0,48 |

Tabla 20-5. Características químicas de las pastas celulósicas obtenidas mediante autohidrólisis- pasteado con etanol

| Temperatura (ºC) | Concentración de etanol (%) | Tiempo (minutos) | (∗)Rendimiento (%) | Índice Kappa | Viscosidad (mL/g) | Holocelulosa (%) | αcelulosa (%) | Lignina Klason (%) |
|---|---|---|---|---|---|---|---|---|
| 145 | 50 | 40 | 65,59 | 69,1 | 354,3 | 63,5 | 43,1 | 19,46 |
| 145 | 70 | 67 | 61,90 | 68,2 | 296,6 | 62,2 | 41,9 | 19,98 |
| 145 | 60 | 94 | 55,52 | 72,1 | 309,9 | 64,7 | 44,1 | 19,21 |
| 145 | 40 | 120 | 55,91 | 69,7 | 331,1 | 74,8 | 53,7 | 17,41 |
| 155 | 60 | 120 | 47,53 | 72,6 | 374,0 | 65,2 | 44,7 | 19,93 |
| 155 | 70 | 40 | 54,33 | 72,8 | 327,9 | 66,0 | 44,1 | 19,99 |
| 155 | 50 | 67 | 57,29 | 73,1 | 414,6 | 63,1 | 42,8 | 18,75 |
| 155 | 40 | 94 | 50,44 | 71,3 | 433,5 | 67,0 | 46,6 | 19,13 |
| 165 | 50 | 120 | 48,60 | 67,9 | 474,9 | 68,6 | 47,1 | 19,50 |
| 165 | 40 | 40 | 51,62 | 70,3 | 438,3 | 66,9 | 48,0 | 18,94 |
| 165 | 60 | 67 | 52,98 | 70,4 | 458,4 | 69,1 | 48,0 | 17,96 |
| 165 | 70 | 94 | 49,05 | 66,2 | 449,9 | 69,3 | 49,3 | 20,38 |
| 175 | 70 | 120 | 41,16 | 63,1 | 551,0 | 71,9 | 53,1 | 18,27 |
| 175 | 60 | 40 | 47,34 | 69,0 | 434,1 | 69,9 | 49,7 | 20,57 |
| 175 | 40 | 67 | 41,67 | 66,1 | 587,1 | 72,6 | 56,7 | 17,42 |
| 175 | 50 | 94 | 42,45 | 65,6 | 573,4 | 69,3 | 49,3 | 20,38 |

(∗) Rendimiento global como suma de los rendimientos de ambas etapas; es decir, cantidad de pasta celulósica obtenida respecto de la materia prima empleada

Tabla 20-6. Propiedades físicas de las hojas obtenidas mediante autohidrólisis-pasteado con etanol

| Temperatura (ºC) | Concentración etanol (%) | Tiempo (min) | Grado de refinado (ºSR) | Longitud de rotura (km) | Alargamiento (%) | Indice de estallido ($kPa\cdot m^2/g$) | Indice de desgarro ($kN\cdot m^2/g$) |
|---|---|---|---|---|---|---|---|
| 145 | 50 | 40 | 35,0 | 2,38 | 1,09 | 0,97 | 1,29 |
| 145 | 70 | 67 | 37,0 | 2,23 | 1,23 | 0,87 | 1,61 |
| 145 | 60 | 94 | 36,5 | 1,99 | 1,45 | 0,82 | 1,44 |
| 145 | 40 | 120 | 38,0 | 2,28 | 1,10 | 0,98 | 1,53 |
| 155 | 60 | 120 | 40,3 | 1,70 | 1,56 | 1,00 | 2,01 |
| 155 | 70 | 40 | 38,3 | 2,46 | 1,57 | 1,17 | 1,57 |
| 155 | 50 | 67 | 37,5 | 2,82 | 1,78 | 1,36 | 1,55 |
| 155 | 40 | 94 | 38,5 | 2,49 | 1,47 | 1,16 | 1,97 |
| 165 | 50 | 120 | 41,4 | 2,37 | 1,89 | 1,23 | 2,73 |
| 165 | 40 | 40 | 39,8 | 2,82 | 1,53 | 1,33 | 2,01 |
| 165 | 60 | 67 | 40,0 | 3,20 | 1,73 | 1,58 | 1,94 |
| 165 | 70 | 94 | 41,0 | 2,61 | 1,29 | 1,19 | 2,04 |
| 175 | 70 | 120 | 43,5 | 1,81 | 0,93 | 1,05 | 2,04 |
| 175 | 60 | 40 | 41,0 | 2,76 | 1,95 | 1,90 | 2,53 |
| 175 | 40 | 67 | 41,0 | 3,85 | 2,03 | 1,36 | 2,10 |
| 175 | 50 | 94 | 41,5 | 2,80 | 1,40 | 1,65 | 2,27 |

Tabla 20-7. Dependencia de las propiedades de las pastas y de las hojas de papel en función de las condiciones de operación en la etapa de pasteado con etanol

| Variable | Ecuaciones |
|---|---|
| Rendimiento (%) | $R = 65{,}64 - 9{,}81\cdot X_T - 4{,}96\cdot X_t + 1{,}92\cdot X_C\cdot X_T + 1{,}89\cdot X_T\cdot X_t$ |
| Índice Kappa | $IK=71{,}86 - 2{,}28\cdot X_T - 0{,}97\cdot X_t - 3{,}047\cdot X_T^2 - 1{,}82\cdot X_T\cdot X_t - 1{,}689\cdot X_C^2$ |
| Viscosidad (mL/g) | $V= 438{,}88 + 105{,}94\cdot X_T - 39{,}23\cdot X_C + 20{,}26\cdot X_t + 9{,}27\cdot X_T^2 + 44{,}11\cdot X_T\cdot X_t - 33{,}37\cdot X_t^2$ |
| Grado Refinado | $ºSR = 38{,}94 + 2{,}59\cdot X_T + 0{,}44\cdot X_C + 1{,}16\cdot X_t - 0{,}45\cdot X_t^2 - 0{,}2\cdot X_T\cdot X_C - 0{,}27\cdot X_T\cdot X_t + 0{,}53\cdot X_C^2 + 0{,}71\cdot X_t^2$ |
| Longitud de rotura (km) | $LR = 2{,}81 + 0{,}37\cdot X_T - 0{,}288\cdot X_C - 0{,}336\cdot X_t - 0{,}177\cdot X_C\cdot X_t - 0{,}489\cdot X_t^2$ |
| Índice de estallido ($kPa\cdot m^2/g$) | $IE =1{,}396 + 0{,}32\cdot X_T - 0{,}166\cdot X_t + 0{,}106\cdot X_T\cdot X_C - 0{,}105\cdot X_T\cdot X_t - 0{,}197\cdot X_C^2 - 0{,}142\cdot X_C\cdot X_t - 0{,}106\cdot X_t^2$ |
| α-celulosa (%) | $\alpha C = 44{,}06 + 3{,}47\cdot X_T - 1{,}275\cdot X_C + 1{,}53\cdot X_t + 2{,}95\cdot X_T^2 - 1{,}64\cdot X_T\cdot X_t + 3{,}46\cdot X_C^2$ |

$X_T$, $X_t$ y $X_C$ son los valores normalizados de la temperatura, tiempo y concentración de etanol, siendo $X_{normalizada}= 2\,(X - X_{media}) / (X_{máxima} - X_{mínima})$, donde X, $X_{media}$, $X_{máxima}$ y $X_{mínima}$ son los valores absolutos de la variable considerada

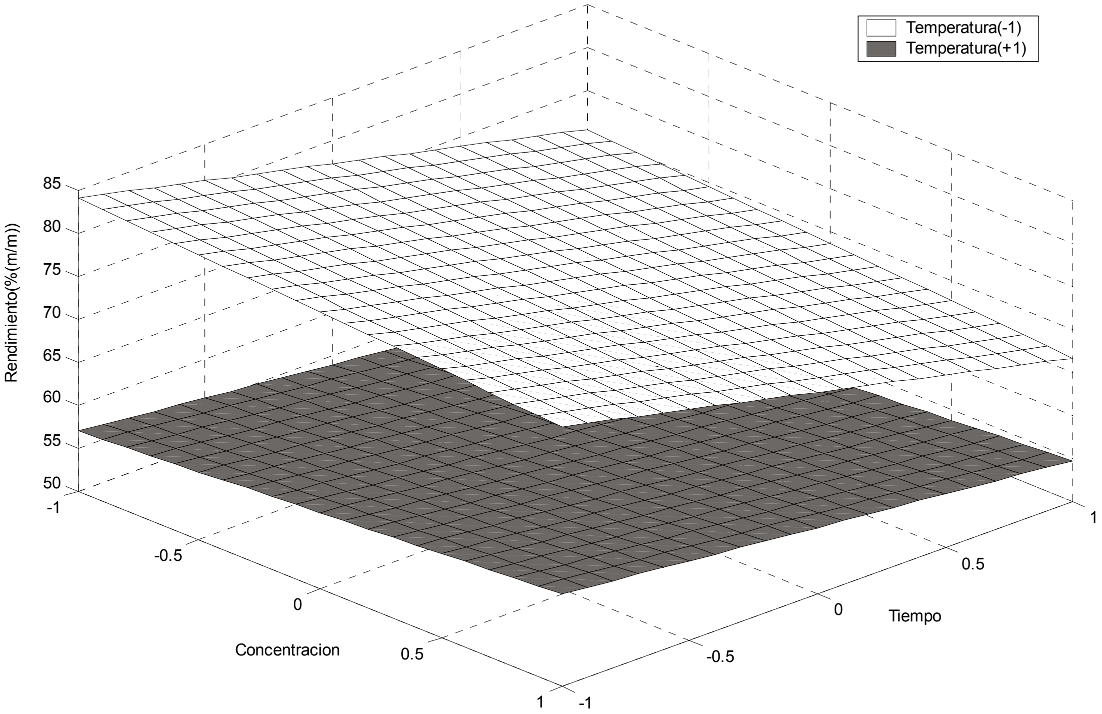

Figura 20-1. Variación del rendimiento con la concentración de etanol y el tiempo a dos niveles de temperatura

# APROVECHAMIENTO ENERGÉTICO E INTEGRADO POR FRACCIONAMIENTO DE BIOMASA LIGNOCELULÓSICA FORESTAL Y AGROINDUSTRIAL. CARACTERIZACIÓN DE HEMICELULOSAS, CELULOSAS Y OTROS PRODUCTOS DEL FRACCIONAMIENTO

## FRACCIONAMIENTO INTEGRAL DE BIOMASA LIGNOCELULÓSICA PARA ENERGÍA Y PRODUCTOS QUÍMICOS

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# APROVECHAMIENTO ENERGÉTICO E INTEGRADO POR FRACCIONAMIENTO DE BIOMASA LIGNOCELULÓSICA FORESTAL Y AGROINDUSTRIAL. CARACTERIZACIÓN DE HEMICELULOSAS, CELULOSAS Y OTROS PRODUCTOS DEL FRACCIONAMIENTO

## Resumen

Se caracteriza la materia prima y de las fases líquidas de la autohidrólisis de 5 materiales lignocelulósicos: *Eucaliptus globulus*, *Arundo donax,* tallos de girasol, tagasaste (*Chamaecytisus proliferus)* y *Paulownia fortunei* para evaluar su viabilidad para la obtención de energía y otros productos químicos a través de un fraccionamiento integral vía autohidrólisis.

De entre los materiales estudiados, los tallos de girasol o el tagasaste presentan unos contenidos en holocelulosa (74,2% y 80,3%) mayores que el *Eucaliptus globulus* y unos contenidos en lignina menores (19,9% y 19,8%). Todas las materias primas superan al *Eucaliptus globulus* por su contenido en xilano (entre 18,3% y 23,9%) pero ninguna alcanza su valor de concentración de glucano (46,8%).

Existe un incremento en la solubilización de las hemicelulosas al aumentar la temperatura de la autohidrólisis con unos óptimos de extracción entre 185ºC y 195ºC para *Arundo donax,* tagasaste o *Paulownia fortunei*, temperatura inferior a la de las mejores condiciones de extracción de *Eucaliptus globulus*. Se obtienen elevados contenidos en oligómeros (tagasaste: 13,9%, tallos de girasol: 21,5%, *Paulownia fortunei*: 11,7%) respecto a *Eucaliptus globulus* (10,3% a 196ºC).

**Palabras clave:** biomasa lignocelulósica, hidrólisis, organosolv, residuos forestales, residuos agrícolas

# FORESTRY AND AGROINDUSTRIAL LIGNOCELULOSIC BIOMASS FOR ENERGY AND CHEMICALS. HEMICELLULOSES, CELLULOSES AND OTHERS BY-PRODUCTS CHARACTERIZATION

## Abstract

Five raw materials and liquors from autohydrolysis process were characterized: *Eucaliptus globulus*, *Arundo donax*, sunflower stalks, tagasaste (*Chamaecytisus proliferus*) and *Paulownia fortunei*, for energy and others chemicals using autohydrolysis and integral fractionation.

Tagasaste and sunflower stalks had holocellulose contents (74,2% and 80,3%) higher than holocellulose content from *Eucaliptus globulus* and lignin contents lower (19,9% y 19,8%) than lignin from *Eucaliptus globulus*. All raw materials had xylan contents (between 18,3% and 23,9%) and glucane contents higher and lower respectively than xyland and glucan from *Eucaliptus globulus* (glucane: 46,8%).

This temperatura is lower than better condition of temperature for Eucalyptus.

Hemicelluloses solubilization were increased with autohydrolysis temperature. The optimal range was 185ºC to 195ºC for *Arundo donax,* tagasaste and *Paulownia fortunei.* This temperature is lower than better condition for *Eucaliptus globulus*. The oligosaccharides contents were high (tagasaste: 13,9%, sunflower stalks: 21,5%, *Paulownia fortunei*: 11,7%) with respect to *Eucaliptus globulus* (10,3% a 196ºC).

**Keywords:** lignocellulosic biomass, hydrolysis, organosolv, forestry residues, agricultural residues

## Introducción

El mundo asiste a un déficit de materias primas, particularmente acuciante en el sector energético, y agravado por las desfavorables implicaciones medioambientales derivadas de una cultura de consumo asentada en la explotación de recursos no renovables. El camino hacia un desarrollo sostenible y renovabilidad de los recursos pasa por la búsqueda/utilización de nuevas fuentes de recursos y productos químicos y de consumo donde la biomasa y en particular la biomasa lignocelulósica se revela como una fuente « necesaria » de materias primas dada su ubicuidad, disponibilidad y carácter « poco contaminante ». Ante el declive de las fuentes de combustibles fósiles, está reconocida como la mayor fuente de energía renovable en el mundo (1, 2, 3) Su aprovechamiento completo (y no solo de fracciones azucaradas o amiláceas para la obtención de etanol vía fermentación, fibrosas para pasta celulósica o combustión completa o de fracciones residuales, etc.) es la única vía para la disposición de una fuente abundante de materias primas en un porcentaje apreciable (4).

Las posibilidades mayoritarias actuales para un aprovechamiento industrial y global del material lignocelulósico pasan por opciones tecnológicas de aprovechamiento energético o bien por el sector de la pasta celulósica y papel. Así, están bien definidas las opciones de:

-Combustión: producción de energía y es el uso más antiguo que la humanidad le ha dado al material lignocelulósico. El rendimiento es bajo (5) pero interesante como fuente energética renovable alternativa a los combustibles fósiles (6, 7). Aunque la combustión libera $CO_2$ que aumenta el efecto invernadero, se considera compensado por la fijación previa mediante la fotosíntesis (8).

-Gasificación: utilizando temperaturas de aproximadamente 750-1000 ºC se gasifica el material, obteniéndose un gas de síntesis para producción de energía con rendimientos del 30-65% (9) o como gas de síntesis para la producción de metanol (de aplicación como combustible para transporte), amoníaco o metano.

-Pirólisis: Destilación seca de la biomasa en medios deficientes en oxígeno a temperaturas del orden de 500 ºC. Se obtiene carbón activo como fase sólida (10) y un aceite pirolítico, con rendimientos que pueden superar el 75% (11), y que se puede emplear como combustible o para posteriores transformaciones químicas.

-Licuefacción: la biomasa se trata en medio acuoso a temperaturas del orden de 300-400 ºC y altas presiones (120-200 bar) durante 5-15 min para obtener una fase líquida con un poder calorífico muy superior al de la biomasa inicial  Los rendimientos energéticos alcanzan el 75% (12).

A este respecto del aprovechamiento energético, se impulsa cada vez más la inclusión del material lignocelulósico entre las fuentes de energía por una conciencia creciente de búsqueda de fuentes alternativas al petróleo y carbón, por aspectos medioambientales, de cambios en países terceros, de seguridad de aprovisionamiento y socioeconómicos relacionados con el sector rural (13). Puede usarse la biomasa vegetal como materia prima para la obtención de otros combustibles como el etanol. Su uso en el transporte sustituyendo a las gasolinas es ecológico, ya que su combustión es limpia (no produce compuestos nitrogenados ni sulfurados) y contribuye a cumplir el protocolo de Kyoto, ya que los ciclos energéticos basados en la utilización de este combustible tienen emisiones de $CO_2$ prácticamente nulas. Además, es fácil su implementación como combustible de transporte sustituyendo desde el 5-20% de la gasolina sin necesidad de realizar adaptaciones en los vehículos.

Además, si la biomasa producida con fines energéticos o para otros productos proviene de "cultivos" forestales o agrarios, se añaden algunas ventajas: se reduce el consumo de combustibles fósiles y, por tanto, no hay aporte nuevo de $CO_2$ a la atmósfera sino que se emite el que se capturó previamente y pueden actuar como sumideros netos si, con la gestión del cultivo, se incrementa el carbono almacenado en el suelo (materia orgánica, hojarasca, raíces, etc.). También, si en los cultivos se utilizan especies que rebrotan y sólo se cosecha la parte aérea dejando en el suelo las raíces y la cepa, las labores del suelo con maquinaria se reducen (y con ello el consumo de energía) hasta que se agote la capacidad de rebrote de la especie.

La alternativa al aprovechamiento global, en un solo proceso (generalmente térmico), de la biomasa lignocelulósica la constituye su aprovechamiento integral, necesariamente por fraccionamiento, que presenta la dificultad de que no es posible la separación de los principales componentes sin degradar la estructura química de algunos de ellos. Dada la compleja estructura, composición y la compleja red de enlaces químicos y físicos no es posible la aplicación de técnicas de separación como la destilación, precipitación, cristalización o extracción (14). La investigación en este campo es muy amplia, diversa, se genera con rápidez y mayoritariamente se centra en aspectos particulares por lo que no es posible sistematizar de forma rigurosa y completa los distintos métodos de fraccionamiento. Rijkens (15) realizó una recopilación de estos métodos, que atendiendo a la principal fracción del material que se degrade se puede distinguir entre métodos de deslignificación (solubilizan lignina) y métodos de hidrólisis (solubilizan polisacáridos). Así, cobra auge la idea de la "biorefinería de material lignocelulósico" capaz de proveer un amplio rango de productos de forma similar a la refinería del petróleo. Muchos esquemas se han probado a escala de laboratorio o piloto, pero todavía no ha sucedido una implementación comercial (16, 17).

La producción de etanol a partir de melazas o almidón es relativamente sencilla, pero si se desea aumentar de modo significativo el uso del etanol como combustible es necesario utilizar los materiales lignocelulósicos, al ser la única fuente suficientemente abundante para sustituir los combustibles fósiles en un porcentaje apreciable (4, 18, 19).

En este marco, las estrategias más prometedoras para una valorización integral por fraccionamiento de la biomasa lignocelulósica orbitan alrededor de la obtención de etanol a partir de productos de hidrólisis dentro de un esquema de « biorefinería ». Este biocombustible o bioetanol es susceptible de uso como combustible para vehículos de transporte (20). Y sería preciso el aprovechamiento de las distintas fracciones poliméricas (lignina, hemicelulosas, celulosas y compuestos valorizables) del material a través de otros productos o subproductos valorizables que compensen los costos de almacenamiento, pretratamiento y tratamientos posteriores. Actualmente, la identificación de los mejores pretratamientos  o etapas de fraccionamiento del material lignocelulósico constituye uno de los campos de trabajo más interesantes de investigación y esfuerzos de desarrollo científico (21).

La justificación de esta temática es obvia por su carácter de renovabilidad y sostenibilidad ambiental y un interés creciente en el aprovechamiento integral y valorización económica de los materiales lignocelulósicos, de los que se puedan obtener:

-Medios fermentables a partir de oligómeros, Xilosa y arabinosa que también pueden fermentarse a productos de alto valor añadido como el etanol (combustible) o el xilitol (22), productos farmaceúticos, pasta para papel, compost, energía…,

-Xilooligómeros. Fracción mayoritaria con aplicaciones alimentarias y farmaceúticas (23) por sus propiedades prebióticas al ser sustrato preferente para las bifidobacterias e inhibir el crecimiento de Clostridium  (24).

-Y productos químicos como la lignina o el furfural que es un intermediario químico para la manufactura de polímeros, alcohol furfurílico y tetrahidrofurano y el principal producto de degradación de las hemicelulosas (25), etc.

La materia prima lignocelulósica es abundante y renovable. Se estima una producción anual entre 10 y 50 billones de toneladas secas (26, 27).

Bajo este esquema de aprovechamiento integral fraccionado se plantean distintas posibilidades según se secuencien etapas de hidrólisis (de hemicelulosas y/o celulosas) y deslignificación.

Optando por una primera etapa de deslignificación, se han usado procesos químicos con disolventes orgánicos a altas temperaturas. Quizá el primero de ellos el pretratamiento con etanol desarrollado en los años 70 por la compañía General Electric para obtener biofuel (28). Como particularidad mencionar la obtención de lignina de alta calidad sin modificar para la que se preveen varias aplicaciones industriales potenciales (29). Con esta idea de utilizar un proceso organosolv con etanol como núcleo de la tecnología para la biorefinería de material lignocelulósico se han descrito procesos como el Lignol, que utiliza temperaturas en el rango de los 200ºC y presiones de 400 psi para extraer la máxima cantidad de lignina de astillas de madera u otra biomasa lignocelulósica. Estos procesos de fraccionamiento basados en un pretratamiento de deslignificación, suelen hacer un énfasis especial en la subsiguiente hidrólisis o sacarificación de la fracción celulósica para obtener medios fermentables para la producción de etanol para combustible (8, 30).

Optando por una primera etapa de pretratamiento de hidrólisis de los polisacáridos, puede clasificarse en:

-Métodos de hidrólisis con ácidos como el tradicional sulfúrico al 72% u otros como el ácido fluorhídrico, trifluoroacético o el clorhídrico (32).

-Métodos enzimáticos para hidrólisis de la celulosa. Que dado el ordenamiento estructural de las moleculas de celulosa es preciso modificar su cristanilidad para favorecer la accesibilidad de las enzimas y que la despolimerización suceda en un tiempo razonable (33).

-Métodos hidrotérmicos. Utilizan agua a elevada temperatura, produciendo la hidrólisis de los grupos acetilo a ácido acético. Este ácido actúa como catalizador produciéndose la solubilización total o parcial de las hemicelulosas (autohidrólisis). Pueden realizarse en dos etapas, una de prehidrólisis de hemicelulosas y otra de hidrólisis de celulosa, o combinarse con una segunda etapa oxidante con algún agente que solubilice la lignina dejando la celulosa en fase sólida y también con algún disolvente orgánico que realize esa deslignificación (34-37).

Con vistas a la integración de la hidrólisis de las hemicelulosas en un proceso más amplio de fraccionamiento integral sería deseable la minimización de la utilización de reactivos químicos externos en las fases de separación. En este sentido cobra ventajas la "autohidrólisis". A elevadas temperaturas, los grupos acetilo del material lignocelulósico originan ácido acético que cataliza la solubilización de las hemicelulosas. En la fase líquida quedan funtamentalmente oligómeros, azúcares, ácido acético, furfural o hidroximetilfurfural y algo de lignina (38).

En este trabajo abordamos la caracterización de materia prima y de las fases líquidas de la autohidrólisis de 5 materiales lignocelulósicos: *Eucaliptus globulus*, *Arundo donax*, tallos de girasol, tagasaste (*Chamaecytisus proliferus)* y *Paulownia fortunei* para evaluar su viabilidad como materias primas, para la obtención de energía y otros productos químicos a través de un fraccionamiento integral vía autohidrólisis

El desarrollo del estudio permitirá establecer como fin último la posibilidad y viabilidad de implantar unos cultivos que permitan disminuir la dependencia exterior de nuestro país en materia energética y de otros productos químicos. También como valor añadido se podrían reducir los excedentes agroalimentarios dando un nuevo uso a parte de los terrenos agrícolas actuales.

## Material y Métodos

### Materias primas

Se han utilizado 5 materias primas: astillas de eucalipto, tallos de girasol (residuo agrícola), podas de tagasaste (leguminosa endémica de las Islas Canarias utilizada como forrajera), paulownia (especie de crecimiento rápido) y *Arundo donax L.* Estas tres últimas cultivadas en parcelas experimentales en el campus de la Rábida de la Universidad de Huelva. Para todos los materiales, y de acuerdo a estudios preliminares, se seleccionaron muestras tamizadas a través de una luz de malla de 8 mm. Estas muestras se acondicionaron y secaron al aire, homogeneizando diferentes lotes y se almacenaron. De los diferentes lotes se tomaron alícuotas para la determinación de la humedad por secado a 105ºC hasta pesada constante.

Para la determinación de la composición química del material lignocelulósico mediante técnicas de cromatografía líquida de alta resolución (HPLC), previamente hay que someter a la materia prima a una hidrólisis ácida cuantitativa en dos etapas, en una primera etapa se utiliza una disolución de $H_2SO_4$ al 72% para romper los polisacáridos a oligómeros. Para ello se toman 0,5 gramos de la materia prima libre de extractos y de humedad conocida (secando a 105ºC hasta pesada constante), molida hasta un tamaño de partícula inferior a 0,5 mm, que se añaden a 5 mL de disolución de ácido sulfúrico al 72%, manteniéndose en un baño de agua a 30±3ºC durante una hora realizando agitaciones periódicas. Pasado ese tiempo se diluye la disolución hasta alcanzar un 4% en ácido sulfúrico, introduciéndose en autoclave durante 1 hora a 121ºC. La disolución se filtra en una placa de poro número 3, obteniendo una fase sólida que permitirá cuantificar la lignina klason, y una fase líquida que será analizada mediante HPLC para determinar su concentración en azúcares (glucosa, xilosa y arabinosa) y ácido acético. A partir de los datos de estas concentraciones, mediante correcciones estequiométricas y teniendo en cuenta la descomposición de azúcares, se puede calcular el contenido de los polímeros que se hidrolizaron para dar lugar a los monómeros medidos en la muestra analizada.

La determinación cromatográfica se llevo a cabo en un cromatógrafo Agilent 1100 HPLC equipado con una columna de resina de intercambio iónico Aminex HPX-87H en las condiciones siguientes: caudal de la fase móvil, 0.05 mol/L de ácido sulfúrico (0,01M); velocidad de flujo, 0.6 mL/min; temperatura de la columna y en el detector, 40 °C y volumen de inyección 5 μL. Todas las muestras analizadas mediante estas técnicas se filtraron a través de membranas de acetato de celulosa de 50 μm de poro.

Procedimiento de autohidrólisis

La autohidrólisis de las materias primas se llevo a cabo con agua en un reactor Parr agitado de 2 L de capacidad con 4 hélices internas para la agitación en condiciones no isotermas. La calefacción se lleva a cabo mediante una manta eléctrica externa. Además, se controla la temperatura automáticamente con un serpentín interno de refrigeración dotado de electroválvulas para abrir el circuito, que también sirve para el enfriamiento del reactor una vez se ha alcanzado la temperatura seleccionada. Se ensayaron temperaturas entre 175°C y 200°C y relaciones líquido/sólido de 8/1 para *Arundo donax*, *Paulownia fortunei* y tallos de girasol y 6/1 para eucalipto y tagasaste (el mínimo que permitía una mezcla homogénea dependiendo del material). Una vez alcanzada la presión normal (barómetro implementado en el reactor), se abre y se separan las fases sólida y líquida por filtración. Una alícuota de la fase sólida se seca a 105°C y con un tamaño de partícula <0,5 mm se somete a caracterización de celulosa (glucano), hemicelulosas (xilano, arabano y grupos acetilo) y lignina usando los mismos métodos que para la materia prima. Una alícuota de la fase líquida, se filtra a través de membranas de 0,45 μm y se inyecta directamente en HPLC para determinar monosacáridos (glucosa, xilosa y arabinosa), furfural, 5 hidroximetil furfural (HMF), ácido acético y ácido fórmico. Una segunda alícuota de la fase líquida (25 mL) se somete a una posthidrólisis cuantitativa con ácido sulfúrico al 4% durante 60 min a 121°C antes del análisis por HPLC. El incremento en las concentraciones de monosacáridos y ácido acético causado por esta posthidrólisis son una medida de la concentración de oligómeros y grupos acetilo unidos a los oligosacáridos.

## Resultados y Discusión

En la tabla 1 se muestra una breve revisión de la composición química de diversos materiales utilizados en la fabricación de pasta celulósica y en la tabla 2 de los cinco materiales lignocelulósicos estudiados en este trabajo: *Eucaliptus globulus*, una de las especies más utilizadas en España para la fabricación de pasta celulósica, tallos de girasol, tagasaste, *Paulownia fortunei* y *Arundo donax*. Este último también muy referenciado en trabajos sobre el sector de la pasta celulósica y el papel.

Pueden utilizarse los resultados de *Eucaliptus globulus* como referencia de comparación al tratarse de un material más estudiado. De hecho, las condiciones metodológicas se basan en el trabajo previo de Garrote (39) sobre este material en el que se planteaban unas condiciones de máxima extracción de oligosacáridos (10,3%) a 196ºC. Son de destacar los bajos contenidos en glucosa y elevados de xilosa en las fases líquidas de la autohidrólisis que indican una importante conservación de la integridad del polímero aún en condiciones de alta temperatura y la mayor capacidad de extración de xilosa de todos los materiales estudiados.

Respecto al tagasaste y los tallos de girasol, puede destacarse que los porcentajes en holocelulosa superan en un 20% y un 10,9% respectivamente, al del eucalipto, y superiores o comparables a los de la paja de trigo (39), *Miscanthus* (40) o los resultados de otros autores sobre *Paulownia* (44, 45). El contenido de glucano y lignina son superiores (20,3% y 38,5% para el glucano y 15,5% y 15,1% para la lignina) en el eucalipto con relación al tagasaste y los tallos de girasol respectivamente. Estos datos permitirían esperar unos mayores rendimientos en oligómeros y xilosa en la fase líquida de la hidrólisis. El contenido en hemicelulosas (holocelulosa-glucano) es muy superior en el tagasaste (41,4%) y en los tallos de girasol (40,4%) respecto al eucalipto (20,1%).

Los contenidos en xilano son similares en el tagasaste, *Miscanthus* (40) y *Arundo donax* con valores comprendidos entre 19% y 19,9% y superiores al valor del eucalipto: 16,6% o 14,2%

(43). Destaca el contenido en xilano de la paja de trigo con un 34,6% (39). De entre los materiales estudiados, los tallos de girasol son los que presentan un mayor contenido en xilano (23,9%). Otros autores (41) obtienen resultados similares en los contenidos en glucano y lignina de *Arundo donax*, aunque sustancialmente inferiores de xilano o arabano.

Los resultados propios sobre caracterización de *Paulownia Fortunei* arrojan diferencias importantes con los de Kalaycioglu et al. (44) o Jiménez et al. (45) salvo los datos de glucano de este último autor (37,4%) comparable al 34,8% del presente trabajo. En parte se pueden atribuir a diferencias climatológicas, de disponibilidad de agua, edad del vegetal y de metodología de análisis que no utilizan cromatografía líquida de alta eficacia. *Paulownia Fortunei* presenta los valores más bajos de holocelulosa y más altos de lignina de todos los materiales estudiados, aunque otros autores (44, 45) presentan valores de holocelulosa (78,8% 71,0%) y de contenido en lignina (22,1%, 22,4%) comparables a otros materiales y mejores que los del eucalipto. Los contenidos en xilano, arabano y grupos acetilo son similares a los encontrados en otros materiales (39-43).

El tratamiento hidrotérmico produce la disolución de los polisacáridos hemicelulósicos presentes en la materia prima. Este proceso se ve favorecido por la acidificación que se produce en el medio por el desprendimiento de los grupos acetilo de las hemicelulosas (43). Esta degradación de los polisacáridos libera los monómeros que los constituyen y como éstos no son totalmente estables en el medio de cocción, a lo largo del proceso pueden formarse furfural e hidroximetilfurfural por deshidratación de las pentosas y de las hexosas respectivamente (46). En los ensayos realizados sólo se han detectado estas sustancias de degradación en pequeñas concentraciones (<0,2 g/L) a las temperaturas más elevadas de los tratamientos de autohidrólisis (195ºC-200ºC).

En la tabla 3 se presentan los resultados de concentración de oligómeros, azúcares y otras sustancias en las fases líquidas de los tratamientos hidrotérmicos. Se presentan cantidades porcentuales de cada compuesto extraídas respecto a la materia prima seca original y porcentajes de extracción de cada fracción sobre esa misma fracción en la materia prima seca original para los cinco materiales lignocelulósicos estudiados. Para los materiales menos referenciados en bibliografía (tagasaste, tallos de girasol y *Paulownia fortunei*) se presentan datos adicionales a temperaturas de hidrólisis por debajo y por encima de las ensayadas con *Eucaliptus globulus* o *Arundo donax* (175ºC a 200ºC).

En general, se observa un incremento en la solubilización al aumentar la temperatura del tratamiento hidrotérmico. En el caso del tagasaste, este incremento es el más acusado. Se incrementa en un factor de 4 la solubilización de oligómeros desde los 175ºC a los 195ºC. La xilosa y el ácido acético presentan también el máximo incremento de la concentración a temperaturas altas, entre 185ºC y 195ºC. Se constata, como apuntábamos antes, un mayor rendimiento en oligómeros en la autohidrólisis del tagasaste respecto del eucalipto en las temperaturas de 185ºC y 195ºC. La arabinosa se ha solubilizado en porcentajes muy acusados respecto a su contenido en la materia prima (95,2% a 195ºC), aunque su presencia en términos absolutos es muy pequeña dado el bajo porcentaje inicial en la materia prima.

En el caso de los tallos de girasol el factor de solubilización de oligómeros aumenta un 28% entre 180ºC y 190ºC para suceder después una disminución a 200ºC que indicaría ya una hidrólisis más extrema hacia azúcares simples u otros productos de descomposición. De hecho, el contenido en ácido acético es muy superior a 200ºC (3,7% respecto a materia prima seca. Concentraciones de 4,6 g/L de ácido acético) al del obtenido con cualquier otro material a cualquier temperatura. Se alcanzaron también concentraciones de 1g/L de ácido fórmico, aunque no se superaron los 0,1g/L de productos de descomposición como el furfural o el 5-hidroximetilfurfural. Se ha constatado el mayor rendimiento en oligómeros respecto al eucalipto y también respecto al tagasaste, 21,5% respecto a materia prima seca y el 90,0% de extracción de oligómeros, los mayores de todos los ensayos.

En el caso de *Paulownia fortunei* el factor de solubilización de oligómeros desde los 180ºC a los 200ºC fue de 1,9, aunque el incremento entre 190ºC y 200ºC es menos acusado y sucede también una disminución en el porcentaje de extraccion de xilosa.

Por otro lado, se comprueba, que en la autohidrólisis del tagasaste en las condiciones más estrictas de temperatura (195ºC), solo un 3,1% de la celulosa presente en la materia prima se ha solubilizado, lo que indica un proceso bastante selectivo donde la celulosa sufre escasa degradación y sería apta para usos posteriores, por ejemplo para la fabricación de pasta celulósica. Las condiciones de operación ensayadas en estos procesos de autohidrólisis no son tan severas como para provocar la solubilización de la celulosa dado que su estructura cristalina de ésta hace que sea más difícil su hidrólisis que en las hemicelulosas (47). Sería un efecto positivo pues permitiría obtener la celulosa poco degradada como un subproducto valorizable (48, 49). El mismo efecto se observa en el resto de materiales y temperaturas ensayadas, donde el porcentaje de glucosa (degradación de la celulosa) no supera el 2,8% en el caso de los tallos de girasol o el 1,6% en el de *Paulownia fortunei*, respecto al contenido de glucano en la materia prima original, aunque no se alcanzan los bajos niveles de degradación de la madera de *Eucaliptus globulus* que no supera el 0,5%.

En comparación con el eucalipto se observa el elevado contenido de oligómeros (tagasaste: 13,9%, tallos de girasol: 21,5%, *Paulownia fortunei*: 11,7%) que se puede obtener con respecto a la materia prima seca operando a la máxima temperatura (195ºC) en el caso del tagasaste o a 190ºC con los tallos de girasol o *Paulownia fortunei*. Las cantidades de oligómeros obtenidos con el tagasaste a temperaturas por debajo de 185ºC (3,3%-9,4%) y tallos de girasol a 180ºC (16,8%) pueden ser superiores a los obtenidos con el eucalipto (8,70%), y es de destacar la escasa presencia de productos de degradación como el furfural en sus licores y en los de la autohidrólisis de *Paulownia fortunei*.

*Arundo donax* ofrece los menores porcentajes de extracción de oligómeros y xilosa además de unos relativamente altos porcentajes de glucosa y ácido acético en la fase líquida de la hidrólisis. Todo ello, haría de *Arundo donax* el material menos apropiado de los estudiados para la explotación de estos procesos de autohidrólisis.

En general, en el caso de la autohidrólisis, tanto de los tallos de girasol como de *Paulownia fortunei*, podría proponerse el rango de temperaturas de 180ºC a 190ºC para minimizar la degradación de la fase sólida a la vez que se maximiza la extracción de xilano. Heitz et al. (50) y Garrote et al. (51) indican como a temperaturas en el entorno de 200ºC sucede una despolimerización importante de la celulosa y decrece el número de fibras de celulosa en el proceso de autohidrólisis.

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## Figuras y tablas

Tabla 1. Composición química de diversos materiales lignocelulósicos (referencias bibliográficas)

| | *Arundo donax*[42] | *Kenaf*[41] | *Aspen*[43] | *Eucalyptus Globulus*[44] | **Paja de trigo**[40] | *Miscanthus*[41] | *Paulownia Fortunei*[45,46] |
|---|---|---|---|---|---|---|---|
| **Glucano, %** | 30,5 | 40,0 | 36,3 | 53,4 | 55,4 | 39,5 | 48,3; 37,4 |
| **Lignina Klason, %** | 15,8-22 | 13,4 | 19,3 | - | | | 22,1; 22,4 |
| **Holocelulosa** | - | - | - | - | 76,2 | 69,4 | 78,8; 71,0 |
| **Xilano, %** | 8,1 | 19,0 | 22,7 | 14,2 | 34,6 | 19,0 | - |
| **Arabano, %** | 0,62 | 1,8 | 0,6 | 0,4 | 5,6 | 1,8 | - |

*Porcentajes respecto a la material prima (100 kg sobre materia seca)

Tabla 2. Composición química del eucalipto, girasol, tagasaste, *Paulownia Fortunei* y *Arundo donax*

| | ***Eucaliptus Globulus*** | **Tallos de girasol** | **Tagasaste** | ***Paulownia Fortunei*** | ***Arundo*** |
|---|---|---|---|---|---|
| **Glucano, %** | 46,8 | 33,8 | 38,9 | 34,2 | 34,8 |
| **Lignina Klason, %** | 22,9 | 19,9 | 19,8 | 27,2 | 23,0 |
| **Holocelulosa** | 66,9 | 74,2 | 80,3 | 56,9 | 64,5 |
| **Xilano, %** | 16,6 | 23,9 | 19,9 | 18,3 | 19,4 |
| **Arabano, %** | 0,54 | 0,37 | 0,63 | 1,13 | 1,50 |
| **Grupos acetilo, %** | 3,49 | 4,32 | 4,39 | 3,31 | 3,40 |

*Porcentajes respecto a la material prima (100 kg sobre materia seca). Valor medio de cuatro replicados

Tabla 3.- Contenido en la fase líquida de oligómeros y monómeros respecto de la materia prima seca original y (/) respecto al contenido en cada fracción de polímero en la materia seca (oligómeros expresados como equivalentes en xilosa)

| **Temperatura hidrotérmico (ºC)** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ***Eucaliptus Globulus*** | | **Tagasaste** | | | ***Arundo donax*** | **Tallos de girasol** | | | ***Paulownia Fortunei*** | | |
| **Porcentaje (%)** | 181ºC | 196ºC (39) | 175ºC | 185ºC | 195ºC | 185ºC | 180ºC | 190ºC | 200ºC | 180ºC | 190ºC | 200ºC |
| **Oligómeros** | 8,70/52,4 | 10,30/62,0 | 3,3/16,6 | 9,4/47,2 | 13,9/69,8 | 2,4/12,4 | 16,79/70,3 | 21,51/90,0 | 18,63/77,9 | 7,8/42,6 | 11,7/63,9 | 14,8/80,9 |
| **Glucosa** | 0,17/0,4 | 0,25/0,5 | 1,1/2,8 | 1,1/2,8 | 1,2/3,1 | 0,89/2,6 | 0,96/2,8 | 0,80/2,4 | 0,56/1,7 | 0,84/2,5 | 0,74/2,2 | 0,56/1,6 |
| **Xilosa** | 1,01/6,1 | 2,21/13,3 | 0,7/3,5 | 0,9/4,5 | 1,7/8,5 | 0,73/3,8 | 1,60/6,7 | 2,08/8,7 | 1,68/7,0 | 0,99/5,4 | 0,74/4,0 | 0,56/3,1 |
| **Arabinosa** | - | - | 0,2/31,7 | 0,4/63,5 | 0,6/95,2 | 0,15/10 | 0,24/64,9 | 0,48/100 | 0,48/100 | 0,38/33,6 | 0,48/42,5 | 0,47/41,6 |
| **Ác. Acético** | 0,21/6,0 | 0,40/11,5 | 0,2/4,6 | 0,4/9,1 | 0,8/18,2 | 1,26/37,1 | 0,88/20,4 | 1,90/44,0 | 3,70/85,6 | 0,40/12,1 | 0,74/22,4 | 0,98/29,6 |

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# Xylooligosaccharides Production from *Arundo donax*

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Samples of *Arundo donax* were subjected to isothermal autohydrolysis, defined by temperature, 150−195 °C; time, 0−15 h; and liquor to solid ratio, 8 g/g. The effect of the operational variables on the yield and composition of both liquid and solid phases obtained after the treatments has been studied. The oligomer concentration and composition have been determined. In the conditions leading to maximum oligomers concentration (defined by dimensionlees time $\theta = 1$) it can be produced up to 17.7 g oligomers/100 g raw material and four acetyl groups/10 xylose monomers. These oligomers are the mean of 50% of nonvolatile compounds. In these conditions, cellulose is almost quantitatively retained in the solid phase, whereas lignin is solubilized at 9%.

**KEYWORDS: Autohydrolysis; hemicelluloses; glucan; lignin; oligomers; *Arundo donax*; xylooligosaccharides; food industry**

## INTRODUCTION

Xylooligosaccharides (XO) may be obtained from lignocellulosic materials (LCM), especially hardwood or agricultural materials, and can also be defined as oligomers, oligosaccharides, substituted oligosaccharides, or xylooligomers. With a chemical perspective, XOs are oligomers of a ramified structure of xylose with a great variety of substituents in the shape of lateral chains of acetyl groups and other components such as uronic acids or arabinose units (*1*−*6*). The degree of XO polymerization is of about 2−20.

XO may be considered as dietary fiber, are nondigestible carbohydrates, and can be used as ingredients of functional foods, regulating the colonic microflora, especially *Bifidobacteria* and *Lactobacilli*, so that their contents increase (*7*−*16*). XOs show advantages in comparison with other oligosaccharides (*10*, *15*). These bacteria show a XO metabolism that produces short-chain fatty acids, compounds with positive healthy effects (*17*, *18*). Other positive effects of XO are their antioxidant activities (*19*−*22*), and XO can be used for the prevention and treatment of several healthy disorders (*23*−*27*). XOs have favorable technological features such as acid stability or heat resistance (*28*). The most important world market is located in Japan, where XOs are prized at about 2500 yen/kg (*29*).

As raw materials, LCM shows several advantages such as their abundance, renewable character, and relatively low cost, which make them useful for their utilization in chemical and food industries. LCMs are composed of cellulose (linear polymer of glucose monomers), hemicelluloses (ramified polymer of monomers such as arabinose, glucose, or xylose and acetyl groups or uronic acids), and lignin (a three-dimensional polymer formed by units of phenyl-propane) and minority fractions (extractable compounds, ashes, etc). Hardwoods and agricultural materials possess a hemicellulosic fraction composed of a structure of xylose with ramifications such as arabinose, acetyl groups, and uronic acids. Because of the high proportion of xylose monomers in theses hemicelluloses, we usually call them xylan. (*30*).

An efficient approach for LCM processes is the “biomass refinery” philosophy (*31*): The LCM is sequentially fractionated to obtain the main components (cellulose, hemicelluloses, and lignin) in separated streams for an individualized profit. The first step in this fractionation can be the autohydrolysis treatment, which can also be named the hydrothermal treatment or hydrothermolysis. Autohydrolysis can solubilize hemicelluloses almost quantitatively (*32*), dropping off the cellulose at solid phase and inducing little modifications in the lignin. The chemical basis of the autohydrolysis processes is the hydrolysis reactions of the hemicelluloses in aqueous medium with temperatures between 150 and 230 °C (*33*), so these reactions are catalyzed by protons. In the initial stages of reaction, the protons proceed from the autoionization of water. The organic acids generated from the raw material such as the acetic acid are the principal source of catalyst in later stages. Reaction mediums are defined by a pH between 3 and 4. The liquid resulting phase is composed principally of hemicellulose byproducts, XOs, monosaccharides, acetic acid, etc. The XOs are the majority reaction products (*34*−*37*) in the operation conditions usually gathered in the bibliography. The resulting solid phase is composed principally by cellulose, lignin, and

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**Table 1.** Composition of *A. donax* L. Used for This Study (Average Values of Four Replicates)

| component | content (weight %, on dry basis) | standard deviation |
|---|---|---|
| glucan | 35.15 | 0.11 |
| xylan | 18.24 | 0.04 |
| arabinan | 0.84 | 0.03 |
| acetyl groups | 3.84 | 0.34 |
| uronic acids | 5.53 | 0.04 |
| Klason lignin | 23.02 | 0.13 |
| extractable compounds | 9.11 | 0.46 |
| ash | 3.06 | 0.15 |

residual hemicelluloses. This phase is susceptible to later treatments such as enzymatic hydrolysis or delignification processes (*10*, *38*, *39*).

This work deals with the study of XO production from *Arundo donax* L. through isothermal autohydrolysis. For this purpose, hydrothermal treatments were carried out, so the operational variables (temperature and reaction time) were varied in the ranges of 150−195 °C and 0−15 h, respectively. Material balances and compositions of solid and liquid phases were evaluated, with special attention to XO concentration and composition.

## MATERIALS AND METHODS

**Raw Material.** *A. donax* L. samples from local plantations were milled to pass an 8 mm screen, since in preliminary studies no diffusional limitations were observed for this particle size; the samples were air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored.

**Analysis of Raw Material and Solid Residues from Hydrothermal Treatment.** Aliquots of raw material or solid residue were milled to particle sizes <0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88) and to quantitative acid hydrolysis with 72% $H_2SO_4$ following standard methods (T-249-cm-85). The solid residue after hydrolysis was recovered by filtration and considered as a Klason lignin. The monosaccharides (glucose, xylose, and arabinose) and acetic acid contained in the hydrolysates were determined by high-performance liquid chromatography (HPLC), as reported elsewhere. Uronic acids were determined spectrophotometrically using galacturonic acid as a standard for quantification (*40*). Ashes were determined by calcination (T-244-om-93). Compositions of raw material are shown in **Table 1**.

**Hydrothermal Processing of Wood Samples.** Raw material and water were mixed in the desired proportions and treated in a 600 cm$^3$ stainless steel reactor (Parr Instruments Company, Moline, IL) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material on a dry basis (the moisture content of the material was considered as water). According to previous works, the influence of LSR is relatively low (*41*). The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle, and cooled by cool water circulating through an internal loop. The reaction media were stirred at 150 rpm and heated to reach the desired temperature; time zero was considered to be the beginning of the isothermal stage.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, and weighed for yield determination. Aliquots of the solid residues were assayed for moisture and composition (duplicate) using the same methods as for raw material analysis. An aliquot of the liquors was oven-dried to constant weight to determine the dry content (DC, g nonvolatile compounds/g liquid phase). A second aliquot was filtered through 0.45 mm membranes and used for direct HPLC determination of monosaccharides, furfural, hydroxymethylfurfural (HMF), and acetic acid. A third aliquot was subjected to quantitative posthydrolysis with 4% $H_2SO_4$ at 121 °C for 45 min, before 0.45 mm membranes filtration and HPLC analysis. The increase in monosaccharide and acetic acid concentrations caused by posthydrolysis provided a measure of the oligomer concentration. HPLC analyses were performed using a BioRad Aminex HPX-87H colum at 30 °C eluted with 0.01 M $H_2SO_4$ at a flow rate of 0.6 mL min$^{-1}$ using a refractive index detector to quantify glucose, xylose, arabinose, acetic acid, HMF, and furfural.

**Table 2.** Operational Conditions Used in This Work

| temperature ($T$, °C) | no. of experiments | time ($t$, h) | time for maximum of oligomers ($t_{MAX}$, h) |
|---|---|---|---|
| 150 | 9 | 0–15 | 8 |
| 165 | 10 | 0–3.33 | 2 |
| 180 | 10 | 0–1.25 | 0.70 |
| 195 | 11 | 0–0.42 | 0.21 |

## RESULTS AND DISCUSSION

**Operational Conditions.** XO is the usual term employed in the bibliography to make reference to the autohydrolysis leading products of LCM with rich xylan hemicelluloses contents. These XOs are oligomers where the principal monomer is the xylose, although they are composed of other sugars such as arabinose and several sugar sustituents such as acetyl groups. In this work, we will use the term oligomer to avoid confusion.

The operational conditions employed in this study (temperature, $T$; and reaction time, $t$) are shown in **Table 2**. The temperature was varied between 150 and 195 °C, and the maximum reaction time was varied between 0.42 and 15 h, values that were selected to study the complete time course of the autohydrolysis process.

$$\theta = \frac{t}{t_{MAX}} \qquad (1)$$

where $t$ is reaction and $t_{MAX}$ is the reaction time of maximum oligomers concentration (shown in **Table 2**).

**Effect of Hydrothermal Treatment on *A. donax* Solubilization.** Having a prior knowledge of the degree of fractionation after the hydrothermal treatment, it would be interesting to study this as it would enable us to carry out an initial evaluation of the treatment efficiency. The variation of the solid yield in the course of dimensionless time is shown in **Figure 1a**. At $\theta = 0$, SY varies between 89.4% at 150 °C and 86.0% at 195 °C. These can be considered relatively low values if they are compared with materials of similar composition such as eucalyptus (*41*). This can be fundamentally justified by the solubilization of the extractable compounds (9.1% of the raw material). This value is much higher than those found in other materials usually employed in the autohydrolysis treatments (*42*).

The SY decreases rapidly up to values of about 65%; then, it decreases more slowly, so a minimal value of 61.4% is reached at $\theta = 2$ and $T = 195$ °C. This minimum closes up to SY 62.4%, which is the value that would be obtained if there was a total solubilization of more influenced fractions by the autohydrolysis treatment. These fractions are hemicelluloses (28.45% of raw material, calculated as the sum of xylan, arabinan, acetyl groups, and uronic acids) and extractable compounds (9.1%). This verifies that cellulose and lignin are not significantly solubilized by the hydrotermal treatment. The raw material solubilization is affected by the temperature, so SY decreases more rapidly at higher temperatures. **Figure 1b** shows evidence of the variation of nonvolatile compounds (NVCs) and volatile compounds (VCs). NVC increases from an initial value of 9.2−10.5% to maximum values at $\theta = 1{-}1.25$, and subsequently, a descent in the aforementioned values is observed. NVC increases with temperature from 21.6% at 150 °C to 25.5% at 195 °C. The

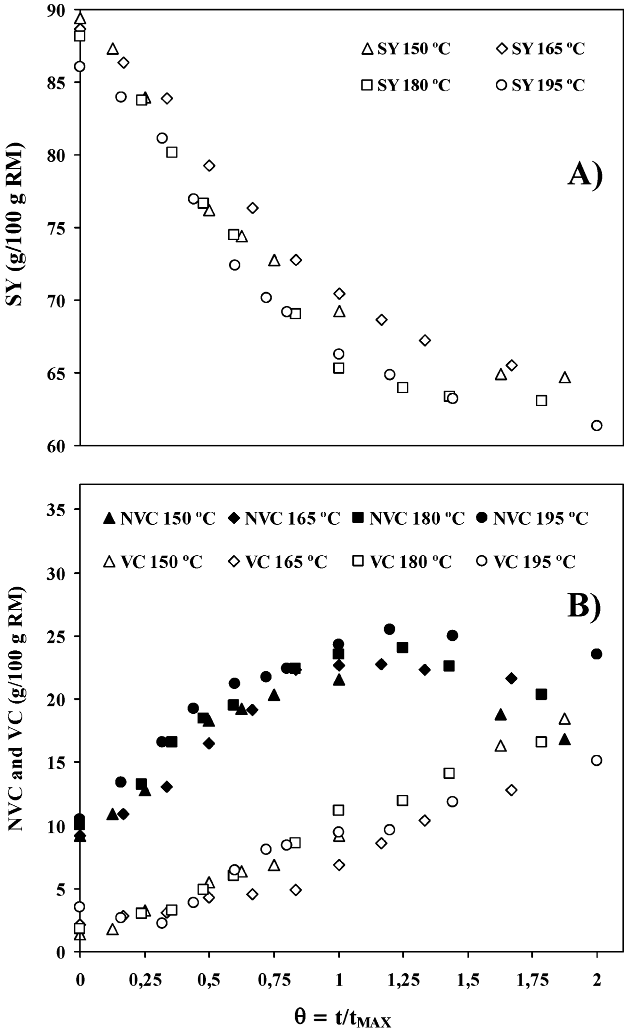

**Figure 1.** Variation with dimensionless $\theta$ of (**a**) SY (solid yield) and (**b**) NVC (nonvolatile compounds) and VCs. Data referred to 100 g of raw material.

content of VCs increases in constant turn from initial values of 2% to maximum values of 18.5%.

**Composition of Solid Phase after Hydrothermal Treatments.** The variation of the composition of the solid phase with respect to $\theta$ after the hydrothermal treatment is shown in **Figure 2** (in weight percent). The cellulosic fraction increases its content from 33.2 to 38.0% at $\theta = 0$ to 50.9−58.1%, so this increase is more rapid up to $\theta = 1-1.2$. The glucan recovery shows that glucan keeps back in the solid phase in a practically quantitative way, with a GnR average value of 95.4%. This minor difference, which is equivalent to 1.6 glucan/100 raw material, can be caused by the solubilization produced by the treatment or the presence of low contents of polymer with glucose. The lignin content increases in a practically linear turn from 26.0 to 26.9% at $\theta = 0$ to 32.7−35.4% at higher times. The Klason lignin recovery decreases from KLR = 100.3−101.9% at $\theta = 0$ to minimum values at $\theta = 1$. These minimum values decreases with temperature, from KLR = 93.0% at $T$ = 150 °C to KLR = 87.1% at $T$ = 195 °C. KLR increases up to 92.3−97.0% when $\theta$ is higher. It can be noted that a minor lignin solubilization, about 10−15% of the initial lignin, is produced and a repolymerizationin in slight proportion takes place at long reaction times. This is a similar behavior to that previously found by Lora and Wayman (*37*). The glucan content in solid residues increases with regards to the initial raw material, which is favorable for a subsequent processing such as enzymatic hydrolysis (due in part to alterations of the structure of the cellulose and partial lignin solubilization) and delignification treatments to produce cellulose pulp and papermaking (justified by a partial degradation of the lignin). These factors are beneficial from the approach of an integral employment of the raw material. The other four fractions (xylan in **Figure 2a**; arabinan, acetyl groups, and uronic acids in **Figure 2b**) compose the hemicelluloses and are shown to be more affected by autohydrolysis. The content of these fourth fractions decreases in constant turn with $\theta$, so lower values are found at high temperatures. Xylan decreases from 18.9 to 22.8% at $\theta = 0$ to 7.0−9.6% at higher times. Arabinan decreases from about 0.8% at $\theta = 0$ to 0% at the highest times. Acetyl groups decrease from 3.5−3.9 to 0.8−1.1% and uronic acids from 5.1−5.3 to 1.2−1.8%. The kinetic patterns of xylan, arabinan, acetyl groups, and uronic acids decompositions are very similar among themselves. The remaining compounds, fundamentally extractable substances, are counted up by difference with the total content (data not show). These compounds show a similar behavior for the four temperatures, decreasing from 6.9 to 7.7% at $\theta = 0$ to practically null values at higher times. This confirms

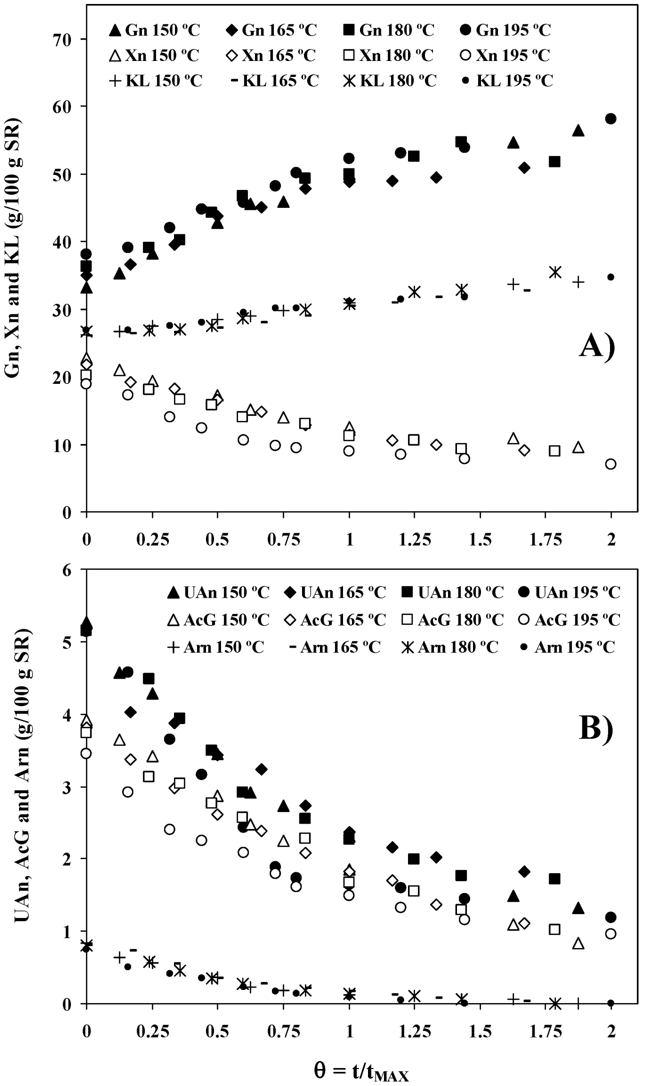

**Figure 2.** Variation with dimensionless $\theta$ of solid-phase composition (see text for variable definitions and units). Data referred to 100 g of solid residue (SR).

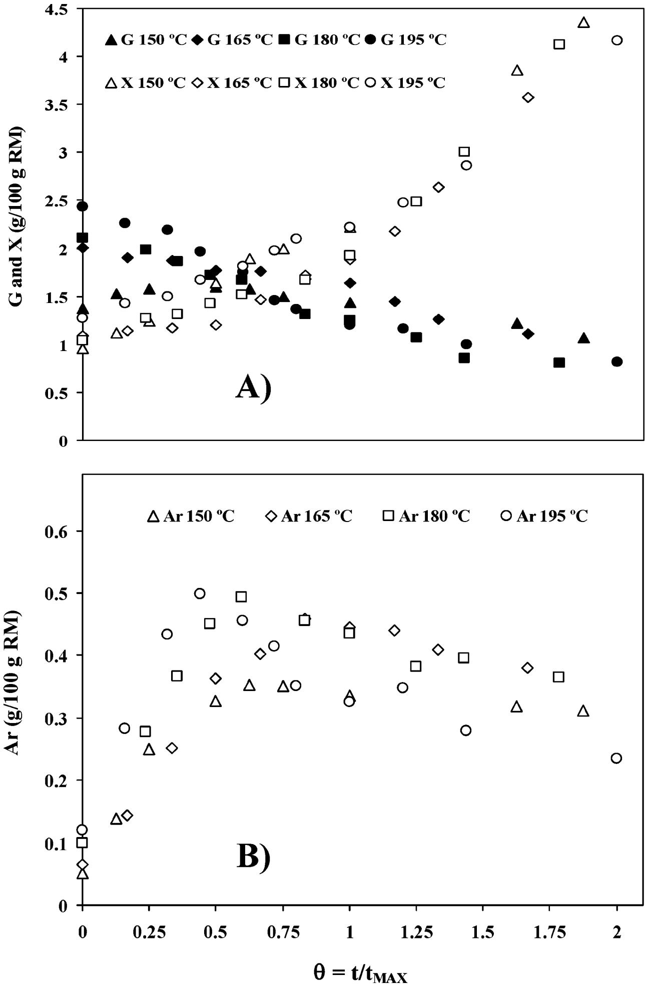

**Figure 3.** Variation with dimensionless $\theta$ of liquid-phase composition of sugars (see text for variable definitions and units). Data referred to 100 g of raw material.

that extractable substances are removed from the solid phase during the hydrothermal treatment.

**Composition of Liquid Phase Obtained in Hydrothermal Treatments: Sugars.** The variation of arabinose, glucose, and xylose concentration in liquid phase with dimensionless time $\theta$ is shown in **Figure 3**. Concentrations of different compounds are expressed as g/100 g raw material on a dry basis to allow an easy comparison with the rest of the data of this work.

The arabinose is very susceptible to hydrolytic degradation. Its content increases from 0.1 g/100 g at $\theta = 0$ to values of 0.4−0.5 g/100 g at $\theta = 0.44-0.83$, which can be considered as a relatively high value if it is compared with the content of the raw material, 0.84 g/100 g, and finally decreases slightly down to 0.3−0.4 g/100 g, probably due to its degradation to furfural. It is remarkable that the maximum arabinose concentration has been found before the maximum concentration of oligomers ($\theta = 1$) take place. At $\theta = 0$, the glucose displays concentrations from 1.4 g/100 g at 150 °C to 2.4 g/100 g at 195 °C; in turn, it decreases when time increases, up to values of about 1 g/100 g. This decrease is very evident at high temperatures. The fact that makes the glucose concentration higher at lower times could be justified by the presence of a low content of hemicellulosic heteropolymers composed by this monomer. If the glucose concentration is passed on to the liquid phase due to the cellulose fraction, its concentration would probably increase with time. Subsequently, the glucose concentration decreases, which is probably caused by its degradation to HMF. The xylose concentration increases in constant turn with time, from 1.0 to 1.3 g/100 g to maximum values of 3.6−4.4 g/100 g at higher times. The xylose increase is higher from $\theta = 1$. The maximum values are much lower than those found for the raw material (18.2 g/100 g), which is justified by the important concentration of oligomers in the liquid phase and the degradation of xylose to furfural.

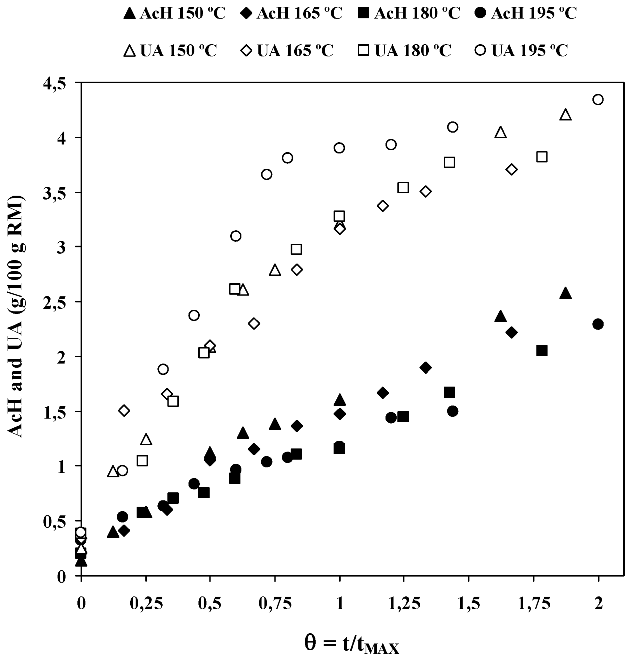

**Figure 4.** Variation with dimensionless $\theta$ of liquid-phase composition of acetic acid and uronics acids. Data referred to 100 g of raw material.

**Composition of Liquid Phase Obtained in Hydrothermal Treatments: Acetic and Uronics Acids.** In **Figure 4**, the variation of the concentration of acetic and uronic acids with dimensionless time $\theta$ can be seen. The acetic acid is produced by the acetyl groups hydrolysis, which is composed of the hemicellulosic fraction, in the shape of substituents of xylose monomers in the solid phase as well as oligomers. The uronic acids calculate by difference between uronic acids in raw material and uronic acids in the solid residue after hydrothermal treatment. The acid acetic concentration increases in constant turn with $\theta$, from 0.1−0.3 g/100 g to 2.0−2.6 g/100 g at the highest times. The generation of acetic acid decreases slightly with an increase of the temperature. The maximum acetic acid concentration is equivalent approximately to two-thirds of the potential acetic acid concentration. The uronic acids increase from 0.3−0.4 g/100 g at $\theta = 0$ to 3.7−4.3 g/100 g at the highest times; an important influence of the temperature is not observed. This increase is quicker to values of about $\theta = 0.75$.

**Composition of Liquid Phase Obtained in Hydrothermal Treatments: Furfural and Hydroxymethylfurfural.** The variation of furfural and HMF concentrations in the liquid phase with dimensionless time ($\theta$) is noted in **Figure 5**. The furfural is generated by the dehydration in acid medium of pentoses, such as arabinose and xylose. It is evident that the concentration of this component increases in constant turn from 0 to maximum values of 0.9−1.6 g/100 g at the highest times, without observing an important influence of temperature. The maximum concentration of the produced furfural means about 8.3% of the pentoses. The HMF is the component generated by the acid dehydration of the hexoses such as the glucose. The behavior of the HMF is very similar to furfural, increasing from 0 to a

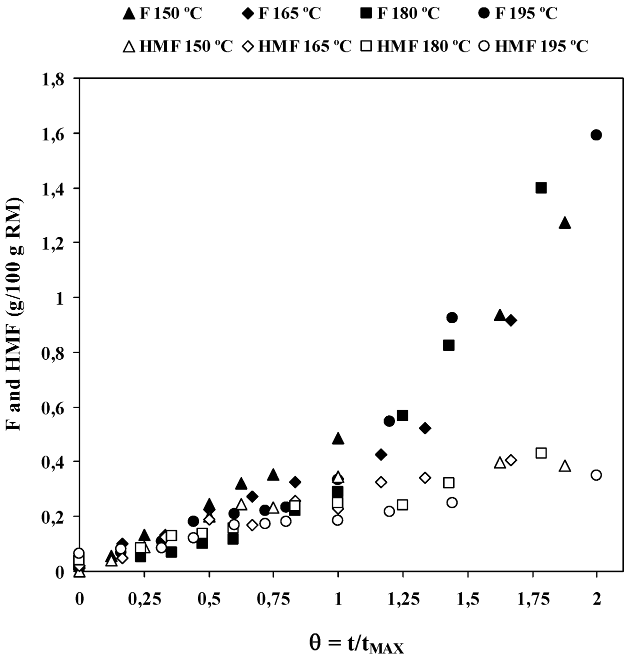

**Figure 5.** Variation with dimensionless $\theta$ of liquid-phase composition of furfural and hydroxymethylfurfural. Data referred to 100 g of raw material.

maximum of 0.3−0.4 g/100 g, which only means about 1.2% of glucan equivalent.

**Composition of Liquid Phase Obtained in Hydrothermal Treatments: Oligomers.** The oligomers are produced by the solubilization of the raw material hemicelluloses in mild acidic media. An increase in reaction time, so that the maximum values are reached at medium times (defined by $\theta = 1$), can be seen. Subsequently, a decrease has been found, justified by the hydrolysis reactions to produce monosacharides and other components such as acetic acid. The oligomer content is counted up measuring every monomer concentration before and after subjecting the liquid phase to an acid posthydrolysis, so an increase of the monomer concentration takes place, which lets us know that the oligomer fraction of a monomer, which is composed of all of the oligomers, and the fraction of itself, which was presented as a monomeric form. In **Figure 6a**, the variation of GO and XO with $\theta$ is plotted, whereas the variation of AcO and ArO is shown in **Figure 6b**.

The XO content increases rapidly from 0 g/100 g at $\theta = 0$ to maximum values at $\theta = 1$ of 11.7 g/100 g at 150 °C, 12.9 g/100 g at 165 °C, 14.5 g/100 g at 180 °C, and 14.2 g/100 g at 195 °C. Then, a decrease is observed up to values of 2.8−6.3 g/100 g at the highest times. The AcO content increases from 0 g/100 g at $\theta = 0$ to its maximum value at $\theta = 1$ and then decreases up to values of 0.6−2.0 g/100 g at the highest times. The kinetic pattern of AcO is similar to that found for XO, but a greater influence of the temperature is found. This is observed at maximum values of AcO, 1.0 g/100 g at 150 °C, 1.5 g/100 g at 165 °C, 2.4 g/100 g at 180 °C, and 2.1 g/100 g at 195 °C, as well as at the average values, 0.6 g/100 g at 150 °C, 0.9 g/100 g at 165 °C, 1.4 g/100 g at 180 °C, and 1.5 g/100 g at 195 °C. The ArO content increases very rapidly from values of about 0 g/100 g at $\theta = 0$ to maximum values of 0.7−0.8 g/100 g. Then, a decrease up to 0 g/100 g is observed in more severe operation conditions. It is remarkable that ArO maximum is obtained at $\theta = 0.25−0.44$, so it increases slightly with temperature. This time is much lower than those found for the other oligomeric fractions, probably caused by its higher reactivity in the hydrolytic medium. In a general sense, a clear tendency of the GO distribution with $\theta$ is not observed. The concentration decreases with the temperature, so it cannot be practically measured at 195 °C. The average content of GO is of about 0.5 g/100 g.

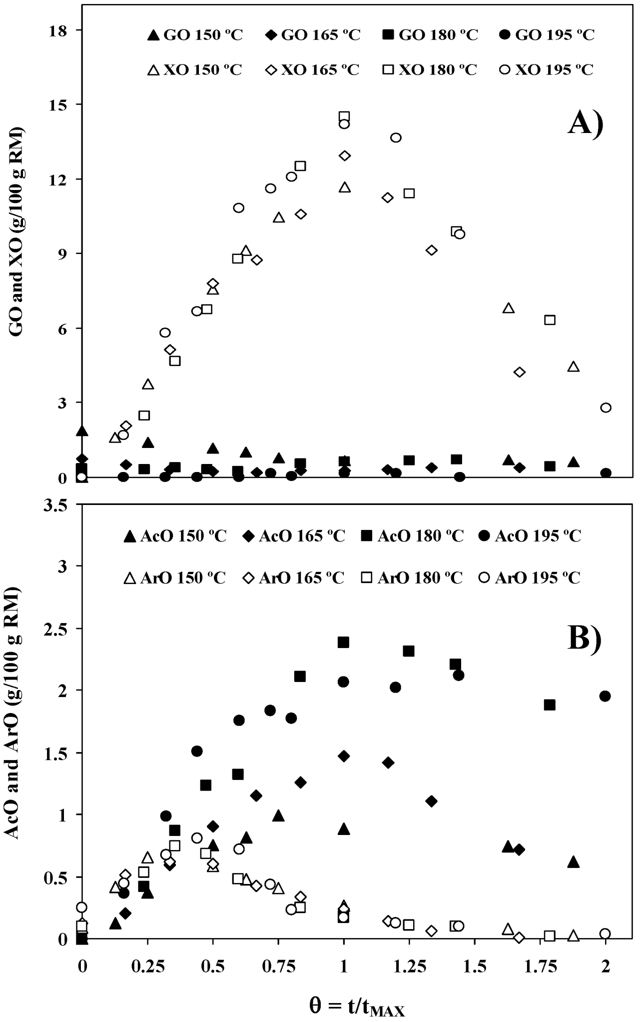

**Figure 6.** Variation with dimensionless $\theta$ of liquid-phase composition of oligomers (see text for variable definitions and units). Data referred to 100 g of raw material.

If global contents of oligomers are calculated, a similar behavior to XO content is found, jusfified by the XO representing the majority fraction. A maximum value of 17.7 g/100 g was reached at $\theta = 1$ and 180 °C. The oligomer contents are expressed as monomer equivalents due to analytical methodology employed in their determination. The distribution and the average molecular weights of oligomers are not determined, so the real values of the oligomer concentrations will be included among 17.7 g/100 g (as monomer equivalents) and 15.2 g/100 (as polymer equivalents).

If the molar compositions of arabinose, glucose, and acetyl groups presented in the oligomers on 10 xylose monomer basis are calculated, it is observed that oligomers are highly composed of arabinose at the first times, with a value of 2.5 arabinose monomers/10 xylose monomers, and then a rapid decrease is observed up to values of about 0.1 arabinose/10 xylose monomers at the highest times. The acetyl groups remain in constant values up to $\theta = 1−1.5$, and then, they increase slightly. The average value of the acetyl substituents increases with the temperature, so it was found to be 0.98, 1.23, 1.94, and 2.29 acetyl groups/10 xylose monomers at temperatures of 150, 165, 180, and 195 °C, respectively. As regards GO

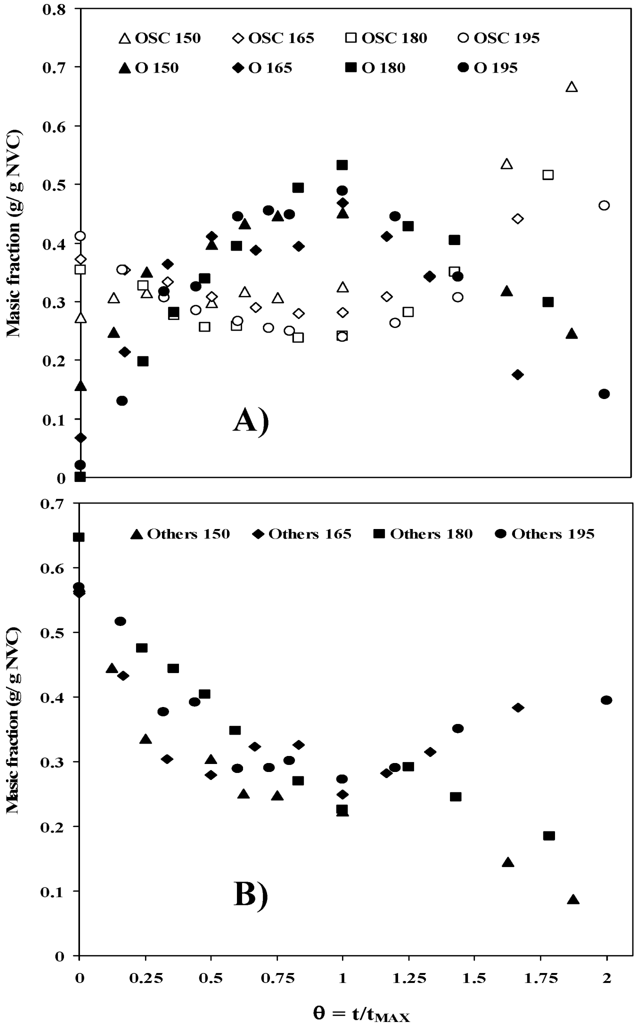

**Figure 7.** Variation with dimensionless $\theta$ of liquid-phase composition of purity (see text for variable definitions and units). Data referred to 1 g of nonvolatile compounds (NVC) in liquid phase.

contents, these are very high at first times, up to 10 glucose monomers/10 xylose monomers, and then, they decrease to minimum values at $\theta = 1$; subsequently, a slight increase is observed.

**Composition of Liquid Phase Obtained in Hydrothermal Treatments: Purity.** The liquid phase is mainly composed of solubilization products from polysaccharides, such as oligomers, sugars, acetic acid, sugar degradation products (furfural and HMF), and nonsaccharide compounds (such as extractable substances, phenolic compounds derived from lignin, and protein-derived compounds). A purity of at least 75% (*28*) is necessary to get a food use. Having knowledge of the distribution of molecular weights in the liquid phase is important to set purification strategies. These compounds have been bunched into three groups (calculated as masic fraction: g substance/g nonvolatile compounds): (i) oligomers (denoted as O), which include AcO, ArO, GO, and XO; (ii) other saccharide compounds (denoted as OSC), which include AcH, Ar, F, G, HMF, and X, OSC also bunch compounds of oligomer hydrolysis (acetic acid, arabinose, glucose, and xylose), compounds of pentose degradation (furfural), and hexoses (HMF); and (iii) others (calculated by difference).

The variation of these variables with dimensionless time $\theta$ is shown in **Figure 7**. The oligomer content increases with $\theta$ up to 0.45−0.53 g oligomers/g NVC at $\theta = 1$ and then decreases, probably caused by breakdown reactions; the maximum oligomer content increases slightly with temperature. Other saccharide compounds decrease from 0.33−0.65 g OSC/g NVC at $\theta = 0$ to 0.24−0.28 g OSC/g NVC at $\theta = 0.75-1$ and then increase quickly to values up to 0.67 g OSC/g NVC, which can be justified by the oligomer hydrolysis, decreasing the global content of nonvolatile compounds. At first times, others comprises up to 0.65 g/g NVC and then decreases rapidly down to $\theta$ of about 0.6; then, it decreases slower, so it increases at high $\theta$ at some temperatures. The others content is 0.22−0.27 g/g NVC at $\theta = 1$.

**Table 3.** Product Distribution in Conditions Leading to Maximum Oligomers Concentration ($\theta = 1$)

| | temperature (°C) | | | |
|---|---|---|---|---|
| | 150 | 165 | 180 | 195 |
| material balances (g/100 g raw material, dry basis) | | | | |
| solid yiel (SY) | 69.3 | 70.5 | 65.3 | 66.2 |
| solubilized fraction (SF) | 30.7 | 29.5 | 34.7 | 33.8 |
| solid-phase composition (g/100 g raw material, dry basis) | | | | |
| glucan content | 34.6 | 34.4 | 32.6 | 34.5 |
| Klason lignin content | 21.4 | 21.4 | 20.1 | 20.6 |
| hemicelluloses content | 11.64 | 11.13 | 10.06 | 8.02 |
| arabinan content | 0.07 | 0.14 | 0.07 | 0.07 |
| xylan content | 8.66 | 8.03 | 7.38 | 5.90 |
| acetyl groups content | 1.32 | 1.27 | 1.11 | 0.99 |
| uronics acids content | 1.59 | 1.69 | 1.50 | 1.06 |
| others compounds content | 1.59 | 3.52 | 2.55 | 3.11 |
| liquid-phase composition (g/100 g raw material, dry basis) | | | | |
| arabinose | 0.34 | 0.44 | 0.43 | 0.33 |
| glucose | 1.43 | 1.64 | 1.25 | 1.20 |
| xylose | 2.22 | 1.88 | 1.92 | 2.22 |
| acetic acid | 1.61 | 1.47 | 1.16 | 1.17 |
| furfural | 0.49 | 0.33 | 0.29 | 0.33 |
| hydroxymethylfurfural | 0.34 | 0.23 | 0.25 | 0.19 |
| total oligomers | 13.8 | 14.9 | 17.7 | 16.6 |
| oligomers composition (monomers/10 xylose monomers) | | | | |
| acetyl groups oligomers | 1.90 | 2.84 | 4.11 | 3.64 |
| arabinose oligomers | 0.23 | 0.19 | 0.12 | 0.12 |
| glucose oligomers | 0.47 | 0.17 | 0.35 | 0.08 |
| liquid-phase purity (g/g nonvolatile compounds) | | | | |
| oligomers (O) | 0.45 | 0.47 | 0.53 | 0.49 |
| others saccharides compounds (OSC) | 0.32 | 0.28 | 0.24 | 0.24 |
| others compounds in liquid phase (others) | 0.22 | 0.25 | 0.23 | 0.27 |

**Compositions in Maximum Oligomers Concentration.** The aim of this work is the oligomer production. With this perspective, **Table 3** summarizes the material balances and product distribution in the conditions leading to maximum oligomer concentrations (defined by $\theta = 1$). Data are expressed as g of substance per 100 of raw material on a dry basis to allow a comparison to be made.

The raw material is solubilized at 33%. With regards to the solid-phase composition, it can be seen that glucan is retained almost quantitatively with an average value of GnR = 97% in the conditions leading to maximum oligomer concentration. The Klason lignin is partially solubilized (average value of KLR = 91%), with the subsequent generation of phenolic compounds, and hemicelluloses are significantly solubilized; the hemicelluloses content decreases from 28.4 to 11.6−8.0 g/100 g raw material. The decrease of total hemicelluloses, xylan, acetyl groups, and uronics acids is higher at elevated temperatures. With regards the contents of other compounds (extractable compounds, ashes, etc), the solubilization that takes place was of about 74−88%.

Regarding the liquid-phase composition, a solubilization of 6 g of other saccharide compounds/100 g raw material and

13.8−17.7 g of oligomers/100 g raw material can be seen. In the oligomer composition, the arabinose and glucose contents are low, with average values of 0.2 and 0.3 monomers/10 xylose monomers, respectively. The acetyl group contents vary in the range of 1.9−4.1 acetyl groups/10 xylose monomers. These values are lower than those found for the raw material, defined by arabinose and acetyl groups contents of 0.5 and 6.5 units/10 xylose monomers, respectively.

The average composition of liquid phase (average values) is 0.49 g oligomers/g NVC, 0.27 g OSC/g NVC, and 0.24 g others/g NVC at $T = 180-195$ °C. The oligomer content is slightly higher, 0.51 g oligomers/g NVC. This information is interesting to evaluate refining strategies; the rest of the substances are fundamentally phenolic compounds and extractable-derived compounds.

## NOTATION

Variables of hydrothermal process: $\theta$ = dimensionless time (dimensionless); $t$ = reaction time (h); $t_{MAX}$ = reaction time of maximum oligomers concentration (h); $T$ = reaction temperature (°C); and LSR = liquor-to-solid ratio (g water/g LCM, on dry basis).

Variables employed to measure the degree of fractionation: SY = solid yield (g solid recovered after autohydrolysis/100 g raw material, on a dry basis); SF = solubilized fraction (g solid solubilized after autohydrolysis/100 g raw material, on a dry basis)

$$\mathrm{SF} = 100 - \mathrm{SY} \tag{2}$$

DC = dry content (g of nonvolatile compounds in liquid phase/g liquid phase); NVC = nonvolatile compounds (g of nonvolatile compounds in liquid phase after autohydrolysis/100 g raw material, on a dry basis)

$$\mathrm{NVC} = \mathrm{DC} \times (\mathrm{LSR} + \mathrm{SF}) \times 100 \tag{3}$$

and VC = volatile compounds (g volatile compounds in liquid phase after autohydrolysis/100 g raw material, on a dry basis)

$$\mathrm{VC} = \mathrm{SF} - \mathrm{NVC} \tag{4}$$

Variables employed to measure solid-phase composition (g/100 g LCM): Gn = glucan content; KL = Klason lignin content; AcG = acetyl groups content; Arn = arabinan content; UAn = uronic acids content; and Xn = xylan content.

Variables employed to measure the degree of fraction recuperation: GnR = glucan recuperation (g glucan in solid residue/100 g glucan in raw material, on a dry basis)

$$\mathrm{GnR} = \frac{\mathrm{Gn}}{\mathrm{Gn_{RM}}} \times \mathrm{SY} \tag{5}$$

KLR = Klason lignin recuperation (g KL in solid residue/100 g KL in raw material, on a dry basis)

$$\mathrm{KLR} = \frac{\mathrm{KL}}{\mathrm{KL_{RM}}} \times \mathrm{SY} \tag{6}$$

where Gn and KL are glucan and Klason lignin contents of solid residues after treatment and the subscript “RM” denotes contents referred to raw material.

Variables employed to measure liquid-phase concentrations and purity: Ar = arabinose concentration (g/100 g raw material); G = glucose concentration (g/100 g raw material); X = xylose concentration (g/100 g raw material); AcH = acetic acid concentration (g/100 g raw material); UA = uronics acids concentration (g/100 g raw material); F = furfural concentration (g/100 g raw material); HMF = hydroxymethylfurfural concentration (g/100 g raw material); ArO = arabinose in oligomers concentration (g of arabinose equivalent/100 g raw material); GO = glucose in oligomers concentration (g of glucose equivalent/100 g raw material); XO = xylose in oligomers concentration (g of xylose equivalent/100 g raw material); AcO = acetyl groups linked to oligomers concentration (g of acetic acid equivalent/100 g raw material); O = total oligomers concentration, calculated as

$$\mathrm{O} = \mathrm{AcO} + \mathrm{ArO} + \mathrm{GO} + \mathrm{XO} \tag{7}$$

and OSC = other saccharide compounds [g saccharide compounds (except oligomers)/g nonvolatile compounds].

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# Comparison of polynomial and neural fuzzy models as applied to the ethanolamine pulping of vine shoots

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## Abstract

The influence of operational variables in the pulping of vine shoots by use of ethanolamine [*viz.* temperature (155–185 °C), cooking time (30–90 min) and ethanolamine concentration (50–70% v/v)] on the properties of the resulting pulp (*viz.* yield, kappa index, viscosity and drainability) was studied.

A central composite factorial design was used in conjunction with the software BMDP and ANFIS Edit Matlab 6.5 to develop polynomial and fuzzy neural models that reproduced the experimental results of the dependent variables with errors less than 10%. Both types of models are therefore effective with a view to simulating the ethanolamine pulping process.

Based on the proposed equations, the best choice is to use values of the operational valuables resulting in near-optimal pulp properties while saving energy and immobilized capital on industrial facilities by using lower temperatures and shorter processing times. One combination leading to near-optimal properties with reduced costs is using a temperature of 180 °C and an ethanolamine concentration of 60% for 60 min, to obtain pulp with a viscosity of 6.13% lower than the maximum value (932.8 ml/g) and a drainability of 5.49% lower than the maximum value (71 °SR).

*Keywords:* Vine shoots; Pulping; Ethanolamine; Polynomial modelling; Neural fuzzy modelling

## 1. Introduction

The production of cellulose pulp generates large amounts of emissions in the cooking of the raw materials. Such emissions are especially polluting when some sulphur-containing reagent is used (*e.g.* in the sulphite and kraft pulping processes). Although the earliest cellulose pulping processes based on sulphur-free organic solvents (*viz.* organosolv processes) were developed long ago, only recently have they been implemented on the pilot plant scale (Asiz and Sarkanen, 1989; Johansson et al., 1987; Jiménez et al., 1997a; Hergert, 1998; Oliet, 1999; Muurinen, 2000), largely as a result of the scarcity of effective alternatives to conventional processes and the need to respond to the new economic and, especially, environmental challenges.

The greatest shortcoming of organosolv processes is that they usually require high pressures, which calls for special equipment and raises operating costs. This makes the use of solvents with a high boiling point (*e.g.* ethanolamine) a potentially interesting alternative.

Raw materials in the range of 92–95% that are used to obtain paper, consist of hardwood or softwood, even though a number of non-wood materials have been shown to provide excellent fibre for speciality paper and are the sole viable raw materials available for this purpose in some geographic areas. Also, non-wood materials may help alleviate the growing scarcity of forest wood materials (Atchinson, 1995, 1996, 1998). These alternative materials include agricultural residues, which are highly abundant

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in Spain (particularly in Andalucía and Castilla-La Mancha). For example, Spain produces roughly one million tons of residual vine shoots each year; at a 50% yield, their processing would provide an amount of pulp equivalent to about 30% of the Spanish total yearly pulp output (Jiménez et al., 1997b; Angulo and García, 2005).

The current pulp production figures a fall short of market demands, which are growing specially fast in developing countries and, to a lesser extent, in some developed countries. This requires establishing new processing plants which, however, should be economical to set up and maintain, and environmentally benign; also, they should provide quality products by efficiently using alternative raw materials (Atchinson, 1995, 1996, 1998; Jiménez et al., 1997b; Angulo and García, 2005). All these requirements can be met by using organosolv processes with non-wood raw materials such as vine shoots.

Since fairly recently, pulping processes have been subjected to factorial design testing in order to develop polynomial models capable of predicting the properties of the pulp (holocellulose, α-cellulose and lignin contents, yield, viscosity and kappa number) and paper sheets (breaking length, stretch, burst index, tear index and brightness), they provide as a function of the operating variables (temperature, time pulping, chemical concentration, liquid/solid ratio and others), with a view to their optimization (Tjeerdsma et al., 1994; Jiménez et al., 1997c,d,1998,1999,2000,2001, 2002,2004; Vega et al., 1997; Gilarranz et al., 1998; Díaz et al., 2004).

Neural fuzzy models, which have proved successfully with non-linear systems as the anaerobic wastewater treatment and the fermentation processes (Works, 1989; Jang, 1993; Jang et al., 1997; Emmanouilides and Petyrou, 1997; Guwy et al., 1997; Tay and Zhang, 1999; Perendeci et al., 2004), have only been employed in this context in the ethanol pulping of Arundo Donax L. (Caparros et al., 2006).

In this work, we examined the influence of the operating variables of the pulping of vine shoots with ethanolamine (*viz.* cooking temperature and time, and ethanolamine concentration) on the properties of the resulting pulp [*viz.* yield, kappa number, viscosity and drainability (as the Shopper–Riegler index)] by using a factorial design. The simulated results provided by second-order polynomial and neural fuzzy models were compared.

## 2. Experimental

### 2.1. Vine shoots

Following air-drying and deleafing, vine shoots were chipped on a semi-industrial wood chipper, the 5–10 mm fraction being isolated by sieving. The shoots contained 67.14% holocellulose, 41.14% α-cellulose, 20.27% lignin, 3.49% ash and 4.87% ethanol–benzene extractables by dry matter weight.

### 2.2. Analysis of the raw material and pulp

Vine shoots were characterized as follows: holocellulose by the (Wise et al. (1946)); and α-cellulose, lignin, ash and ethanol–benzene extractables according to TAPPI 203 os-61, TAPPI 222, TAPPI 211 and TAPPI 204. The viscosity, kappa index and drainability (Shopper–Riegler index) of the pulp were determined according to ISO 5351/1, UNE 57-034 and UNE 57-039, respectively. Pulp yield was determined by weighing.

### 2.3. Pulping

Pulp was obtained by using a 15-L batch cylindrical reactor that was heated by means of an electrical wire and linked through a rotary axle – to ensure proper agitation – to a control unit including a motor actuating the reactor and the required instruments for measurement and control of pressure and temperature.

Once the raw material was cooked in the reactor, the mass was fiberized in a wet disintegrator at 1200 rpm for 30 min and the screenings were separated by sieving through a screen of 1 mm mesh size. The pulp thus obtained was beaten in a Sprout–Waldron refiner.

### 2.4. Experimental design

The $2^n$ factorial design used (Montgomery, 1991) consisted of a series of points (experiments) around a central one (central experiment, in the centre of a cube) and several additional points (additional experiments lying at the cube vertices and side centres).

### 2.5. Polynomial modelling

Experimental data were fitted to the following second-order polynomial:

$$\mathrm{Ye} = a_0 + a_1X_T + a_2X_t + a_3X_E + a_{11}X_T^2 + a_{22}X_t^2 + a_{33}X_E^2 + a_{12}X_TX_t + a_{13}X_TX_E + a_{23}X_tX_E \tag{1}$$

where Ye denotes the response variables [*viz.* yield (YI), kappa index (KI), viscosity (VI) or drainability (DR)]; $X_T$, $X_t$ and $X_E$ are the normalized values of the operational variables (temperature, time and ethanolamine concentration, respectively); and $a_0$–$a_{23}$ are constants.

The values of the operational variables were normalized to values from −1 to +1 by using the following expression:

$$X_\mathrm{n} = \frac{2\cdot(X-\overline{X})}{X_\mathrm{max}-X_\mathrm{min}} \tag{2}$$

where $X_\mathrm{n}$ is the normalized value of temperature ($T$), time ($t$) or ethanolamine concentration ($E$); $X$ is the absolute experimental value of the variable concerned; $\overline{X}$ is the mean of $X_\mathrm{max}$ and $X_\mathrm{min}$; and $X_\mathrm{max}$ and $X_\mathrm{min}$ are the maximum and minimum values, respectively, of such a variable.

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### 2.6. Neural fuzzy modeling

The integration of fuzzy systems (Zadeh, 1965) and neural networks (Works, 1989) combines the advantages of the two systems and provides an especially powerful modelling tool, *viz.* the neural fuzzy system, which uses neural networks as tools in fuzzy systems.

The variation of pulp properties as a function of the operational variables of the pulping process can be predicted by using the following expression (Jang et al., 1997):

$$Y_{\mathrm{e}} = \frac{\sum_{l=1}^{m} y^l \cdot \left[\prod_{i=1}^{n} \mu_{\mathrm{Fi}}^l(x_i, \theta_i^l)\right]}{\sum_{l=1}^{m} \left[\prod_{i=1}^{n} \mu_{\mathrm{Fi}}^l(x_i, \theta_i^l)\right]} \qquad (3)$$

where

| | |
|---|---|
| $Y_{\mathrm{e}}$ | is the estimate value of output variable, |
| $m$ | the number of rules, |
| $n$ | the number of input variables, |
| $y^l$ | the defuzzifier and, |
| $\mu_{\mathrm{Fi}}^l(x_i, \theta_i^l)$ | the membership-function. |

In this paper, $[\prod_{i=1}^{n} \mu_{\mathrm{Fi}}^l(x_i, \theta_i^l)]$ will be denoted by $R_l$ which is known as a fuzzy rule.

In this sense, $R_l$ is defined by the product of $n$ membership functions (one per independent variable). Then, Eq. (3) could be expressed as

$$Y_{\mathrm{e}} = \frac{\sum_{l=1}^{m} y^l \cdot R_l}{\sum_{l=1}^{m} R_l} \qquad (4)$$

Three operational variables – our case –, two levels per independent variable and the use of a singleton defuzzifier (a constant parameter; $c_l$) allow Eq. (3) to be developed to:

$$Y_{\mathrm{e}} = \frac{\sum_{l=1}^{8} c_l \cdot R_l}{\sum_{l=1}^{8} R_l} \qquad (5)$$

Linear membership functions are selected for independent variables with two levels. The mathematical equations which respond to linear membership functions are

$$\mu(\mathrm{low}) = 1 - \frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}(x - x_{\mathrm{low}}) \qquad (6)$$

$$\mu(\mathrm{high}) = \frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}(x - x_{\mathrm{low}}) \qquad (7)$$

where $x_{\mathrm{high}}$ is 185 °C, 90 min or 70%, and $x_{\mathrm{low}}$ is 155 °C, 30 min or 50%, for temperature, time and ethanolamine concentration, respectively.

With three independent variables, the combination of the membership functions provides eight fuzzy rules according to the extreme (high and low) values of such variables. This combination could be

R1: low $T$, low $t$ and low $E$
R2: low $T$, low $t$ and high $E$
R3: low $T$, high $t$ and low $E$
R4: low $T$, high $t$ and high $E$
R5: high $T$, low $t$ and low $E$
R6: high $T$, low $t$ and high $E$
R7: low $T$, high $t$ and high $E$
R8: high $T$, high $t$ and high $E$

Independent variables with three levels (low, medium and high) are selected in order to get improve the fitness of the experimental values. In this sense, Gaussian membership functions for variables with three levels have been selected to perform the response of the system since they provide the best results at validating the model. Three

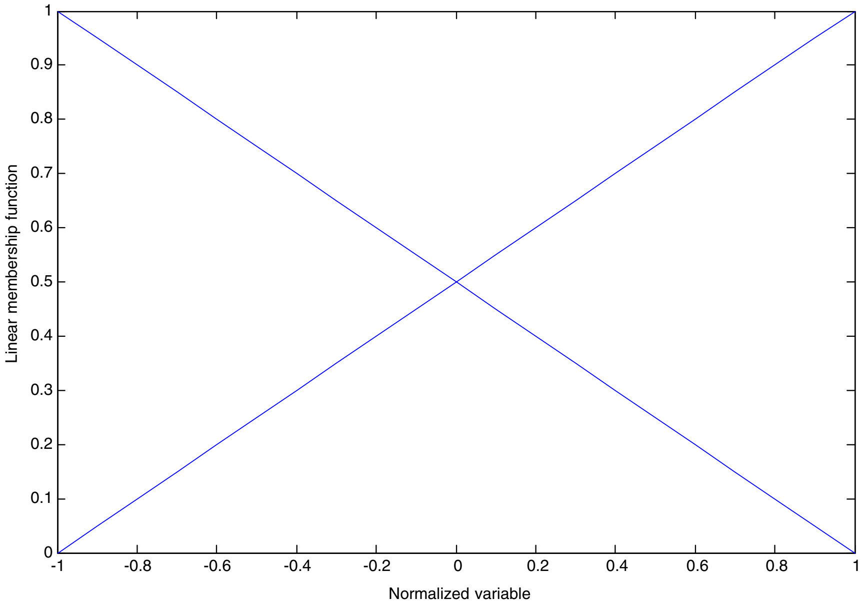

Fig. 1. Uniform distribution of linear membership functions.

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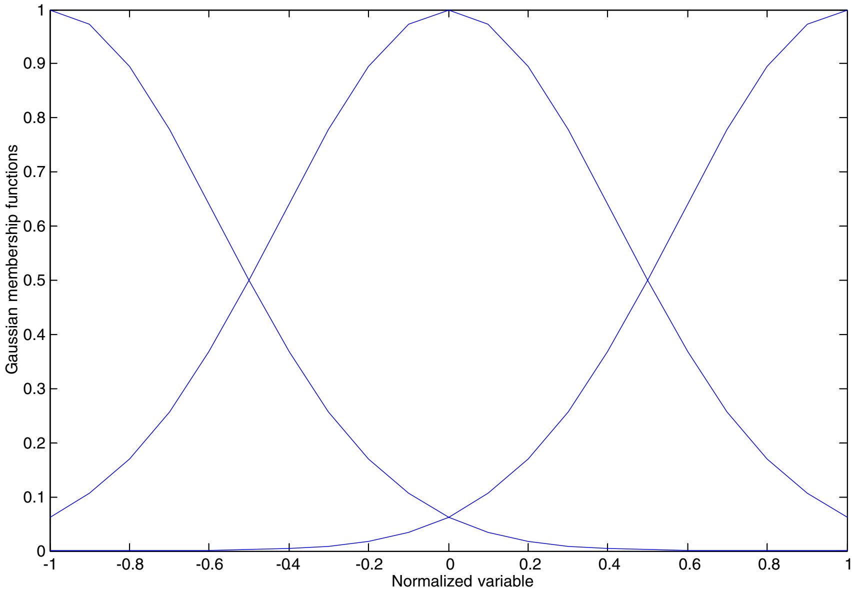

Fig. 2. Uniform distribution of Gaussian membership functions.

levels for one independent variable and two levels for the others allow Eq. (3) to be developed to

$$Y_{\mathrm{e}} = \frac{\sum_{l=1}^{12} c_l \cdot R_l}{\sum_{l=1}^{12} R_l} \tag{8}$$

The mathematical equations which respond to Gaussian membership functions are

$$\mu(\text{low}) = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{low}}}{L}\right)^2\right) \tag{9}$$

$$\mu(\text{medium}) = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{medium}}}{L}\right)^2\right) \tag{10}$$

$$\mu(\text{high}) = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{high}}}{L}\right)^2\right) \tag{11}$$

where $x_{\text{low}}$, $x_{\text{medium}}$ and $x_{\text{high}}$ are the low, medium and high values of the temperature (155, 170 and 185 °C), time (30, 60 and 90 min) and ethanolamine concentration (50, 60 and 70%).

The introduction of three levels for a variable is justified since a high increase on the fitness is observed by introducing those for one specific variable and not for the others. The proposed combinations of the membership functions are clearly defined in the tables exposed in the result section.

The parameters and constants in the previous equation were estimated by using the ANFIS (Adaptative Neural Fuzzy Inference System) Edit tool in the Matlab 6.5 software suite. In that form, membership function parameters are not trained since they have previously been defined in order to provide a uniform distribution of the membership function within the independent variable range. In this sense, Fig. 1 shows a uniform distribution for a normalized variable using linear membership functions. Fig. 2 shows such uniform distribution for Gaussian membership functions. The constants $c_l$ are trained in order to minimize the mean square error.

## 3. Experimental results and discussion

Table 1 shows the experimental values of the pulp properties, which differed by less than 5–10% from their means as obtained in triplicate measures.

### 3.1. Polynomial modelling

The experimental results were fitted to a polynomial model by multiple regression using the software BMDP.

Table 1
Experimental values of the properties of pulp obtained by ethanolamine pulping of vine shoots

| Temperature (°C), time (min) and ethanolamine (%) | Yield (%) | Kappa index | Viscosity (mL/g) | Drainability (°SR) |
|---|---|---|---|---|
| 185, 90, 70 | 32.41 | 29.46 | 801.5 | 73.0 |
| 155, 30, 50 | 63.95 | 94.65 | 711.0 | 54.5 |
| 155, 90, 70 | 36.30 | 53.67 | 883.0 | 61.0 |
| 170, 60, 60 | 36.11 | 44.70 | 900.7 | 62.0 |
| 185, 90, 50 | 33.13 | 40.29 | 801.0 | 66.0 |
| 170, 30, 60 | 37.66 | 53.51 | 889.5 | 66.0 |
| 155, 90, 50 | 43.61 | 72.43 | 767.6 | 68.5 |
| 170, 60, 70 | 35.27 | 37.70 | 930.2 | 68.0 |
| 170, 90, 60 | 34.81 | 34.76 | 899.6 | 69.0 |
| 185, 30, 70 | 34.17 | 39.35 | 858.2 | 65.5 |
| 170, 60, 50 | 37.28 | 55.03 | 880.0 | 69.0 |
| 185, 60, 60 | 35.77 | 38.01 | 836.6 | 67.5 |
| 155, 30, 70 | 53.03 | 66.92 | 842.0 | 60.0 |
| 155, 60, 60 | 44.49 | 78.36 | 772.8 | 58.0 |
| 185, 30, 50 | 36.79 | 49.79 | 881.5 | 64.0 |

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Table 2
Polynomial models for the properties of pulp obtained by ethanolamine pulping of vine shoots

| Dependent variable | Values of the constants in the polynomial equations | | | | | | | Values of $p$ and Student $t$-test | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_{11}$ | $a_{12}$ | $a_{13}$ | $<p$ | $>t$ |
| Yield (%) | +36.23 | −6.91 | −4.53 | −2.36 | +3.96 | +1.86 | | 0.0751 | 2.05 |
| Kappa index | +45.14 | −16.91 | −7.36 | −8.51 | +11.15 | – | +3.13 | 0.0274 | 2.63 |
| Viscosity (mL/g) | +900.0 | +20.2 | – | +27.4 | −84.5 | −29.6 | −33.7 | 0.0004 | 5.53 |
| Drainability (°SR) | +64.8 | +3.4 | −2.8 | – | – | – | – | 0.0275 | 2.51 |

[Values of the constants in the polynomial equations.]

Table 3
Values of the operational variables required to ensure optimal properties in pulp obtained by ethanolamine pulping of vine shoots

| Dependent variable | Optimum (maximum or minimum*) value of the dependent variable | Values of the operational variables required to obtain the optimum values of the dependent variables | | |
|---|---|---|---|---|
| | | $X_T$ | $X_t$ | $X_E$ |
| Yield (%) | 55.85 | −1 | −1 | −1 |
| Kappa index | 25.02* | +0.62 | +1 | +1 |
| Viscosity (mL/g) | 932.8 | −0.25 | +1 | +1 |
| Drainability (°SR) | 71.0 | +1 | −1 | – |

Table 4
Maximum changes in the dependent variables with changes in one operational variable on constancy of the others (the percent differences from the changes are given in brackets)

| Equation | Variation with the operational variable | | |
|---|---|---|---|
| | Temperature | Time | Ethanolamine concentration |
| Yield (%) | 25.46 | 16.98 | 8.44 |
| | (41.74) | (2.84) | (13.84) |
| Kappa index | 29.17 | 14.72 | 13.12 |
| | (116.59) | (58.79) | (52.40) |
| Viscosity (mL/g) | 132.8 | 14.7 | 71.6 |
| | (14.2) | (1.6) | (7.7) |
| Drainability (°SR) | 3.40 | 2.75 | – |
| | (4.79) | (3.88) | |

Those terms possessing a Snedecor $F$-value greater than 3.0 and a Student $t$-value greater than two were deemed statistically significant. Table 2 gives the coefficients of the different terms in the equations, as well as the highest p and lowest Student $t$-values for the terms.

The predictions of the previous equations reproduced the experimental results for the dependent variables with errors less than 3–9%.

The values of the operational variables providing the best pulp properties (yield, kappa index, viscosity and drainability) were identified by using multiple non-linear programming as implemented in the method of More and Toraldo (1989). Table 3 shows the optimum values of the dependent variables and those of the operational variables required to obtain them.

The polynomial equations allow one to identify the operational variables most markedly influencing the pulp properties. The maximum variations in the dependent variables with changes in the operational variables over the studied range were obtained by altering one independent variable at a time while keeping all others constant. The results are shown in Table 4 together with the maximum percent differences in the dependent variables from their optimum values over the studied variation ranges.

Polynomial models (Table 2) can be used to select values of the operational variables providing near-optimal pulp properties (Table 3) while saving energy and immobilized

Table 5
Values of the constants $c_i$ in the neural fuzzy model for the pulp properties

| Rule | Operational variables | | | Dependent variables | | | |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (min) | Ethanolamine (%) | Yield (%) | Kappa index | Viscosity (mL/g) | Drainability (°SR) |
| 1 | Low 155 | Low 30 | Low 50 | 63.89 | 91.95 | 692.9 | 55.42 |
| 2 | Low 155 | Low 30 | High 70 | 52.50 | 65.14 | 829.1 | 60.42 |
| 3 | Low 155 | High 90 | Low 50 | 42.88 | 71.04 | 752.3 | 68.85 |
| 4 | Low 155 | High 90 | High 70 | 35.27 | 52.81 | 871.9 | 60.79 |
| 5 | High 185 | Low 30 | Low 50 | 37.14 | 46.98 | 880.5 | 65.65 |
| 6 | High 185 | Low 30 | High 70 | 34.44 | 36.89 | 852.5 | 66.61 |
| 7 | High 185 | High 90 | Low 50 | 33.38 | 38.15 | 794.1 | 67.02 |
| 8 | High 185 | High 90 | High 70 | 32.68 | 27.77 | 791.4 | 73.49 |
| 9 | Medium 170 | Low 30 | Low 50 | 36.62 | 51.70 | 878.7 | – |
| 10 | Medium 170 | Low 30 | High 70 | 35.10 | 39.74 | 928.6 | – |
| 11 | Medium 170 | High 90 | Low 50 | 35.11 | 38.95 | 891.1 | – |
| 12 | Medium 170 | High 90 | High 70 | 33.88 | 27.63 | 941.5 | – |
| $R^{2}$[a] | | | | 0.99 | 0.99 | 0.99 | 0.91 |
| $L$[b] | | | | 6.36 | 6.36 | 6.36 | – |

[a] $R^2$ = regression coefficient.

[b] $L$ = width of the Gaussian distribution.

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Table 6
Values of the dependent variables as estimated with the neural fuzzy models and deviations from their experimental counterparts (in brackets)

| Temperature (°C), time (min) and ethanolamine (%) | Yield (%) | Kappa index | Viscosity (mL/g) | Drainability (°SR) |
|---|---|---|---|---|
| 185, 90, 70 | 32.73 (0.98) | 27.74 (5.70) | 800.3 (0.15) | 73.49 (0.67) |
| 155, 30, 50 | 63.04 (1.42) | 91.50 (3.33) | 703.6 (0.99) | 55.42 (1.69) |
| 155, 90, 70 | 35.23 (2.96) | 52.53 (2.13) | 876.0 (0.79) | 60.79 (0.34) |
| 170, 60, 60 | 36.22 (0.30) | 43.63 (2.39) | 898.7 (0.22) | 64.78 (4.49) |
| 185, 90, 50 | 33.45 (0.97) | 38.19 (5.22) | 799.9 (0.14) | 67.02 (1.65) |
| 170, 30, 60 | 37.65 (0.02) | 50.06 (6.44) | 893.7 (0.46) | 62.03 (6.02) |
| 155, 90, 50 | 42.64 (2.23) | 70.68 (2.42) | 760.6 (0.92) | 68.85 (0.51) |
| 170, 60, 70 | 35.20 (0.20) | 37.09 (1.61) | 924.1 (0.72) | 65.33 (3.93) |
| 170, 90, 60 | 34.79 (0.06) | 37.20 (7.01) | 903.7 (0.46) | 67.54 (2.12) |
| 185, 30, 70 | 34.47 (0.87) | 36.97 (6.06) | 857.0 (0.14) | 66.61 (1.69) |
| 170, 60, 50 | 37.24 (0.10) | 50.17 (8.84) | 873.3 (0.76) | 64.24 (6.91) |
| 185, 60, 60 | 34.44 (3.71) | 37.51 (1.32) | 834.4 (0.26) | 68.19 (1.03) |
| 155, 30, 70 | 51.96 (2.02) | 64.60 (3.09) | 835.0 (0.83) | 60.42 (0.70) |
| 155, 60, 60 | 48.22 (8.37) | 69.89 (10.81) | 793.9 (2.73) | 61.37 (5.81) |
| 185, 30, 50 | 37.12 (0.90) | 47.11 (5.39) | 880.4 (0.13) | 65.65 (2.58) |

Table 7
Experiments used to validate the neural fuzzy models for the pulping of vine shoots with ethanolamine

| Dependent variable | Experiment 16 ($T = 162.5$ °C; $t = 45$ min; $E = 55\%$) | | | Experiment 17 ($T = 177.5$ °C; $t = 75$ min; $E = 65\%$) | | | Experiment 18 ($T = 177.5$ °C; $t = 60$ min; $E = 55\%$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Experimental value | Estimated value | Deviation (%) | Experimental value | Estimated value | Deviation (%) | Experimental value | Estimated value | Deviation (%) |
| YI (%) | 45.00 | 47.50 | 5.56 | 32.50 | 33.99 | 4.58 | 35.05 | 35.24 | 0.55 |
| KI | 66.05 | 69.64 | 5.43 | 31.85 | 33.54 | 5.30 | 43.10 | 41.75 | 3.13 |
| VI (mL/g) | 829.5 | 817.8 | 1.41 | 898.9 | 867.4 | 3.51 | 866.7 | 865.3 | 0.16 |
| DR (°SR) | 60.0 | 61.1 | 1.76 | 68.5 | 68.3 | 0.22 | 65.0 | 65.9 | 1.36 |

$T$, $t$ y $E$ = Temperature (°C), time (min) and ethanolamine concentration (%); YI = Yield; KI = kappa index; VI = Viscosity; DR = Drainability.

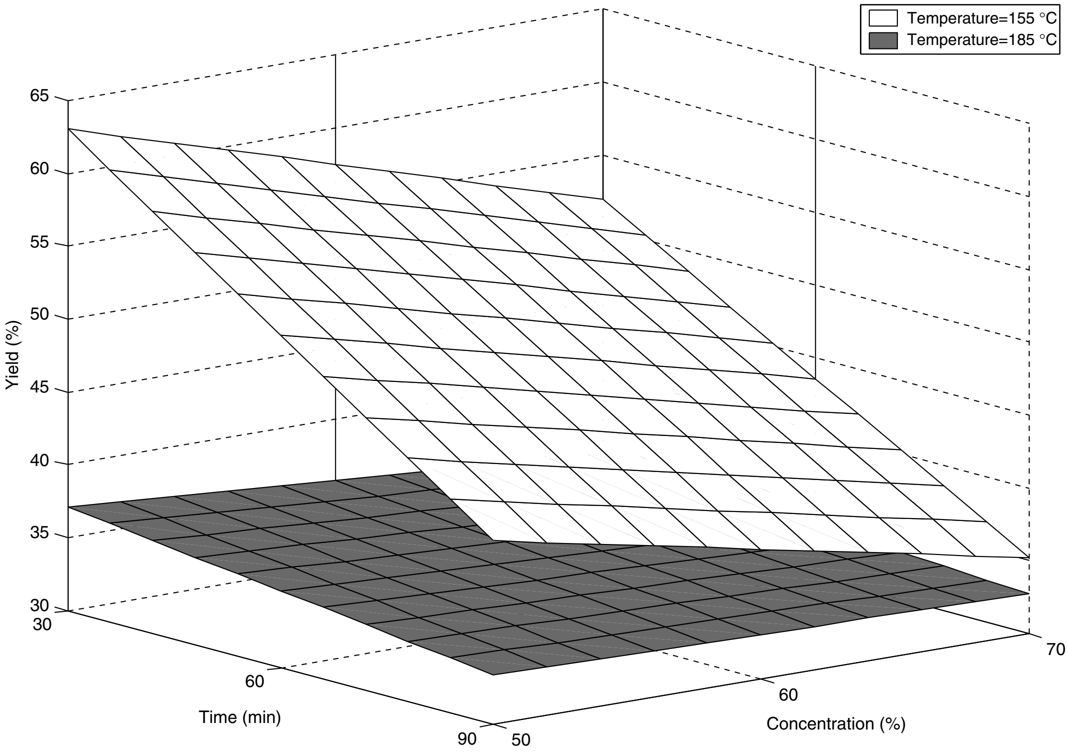

Fig. 3. Variation of pulp yield with time and ethanolamine concentration at extreme temperatures.

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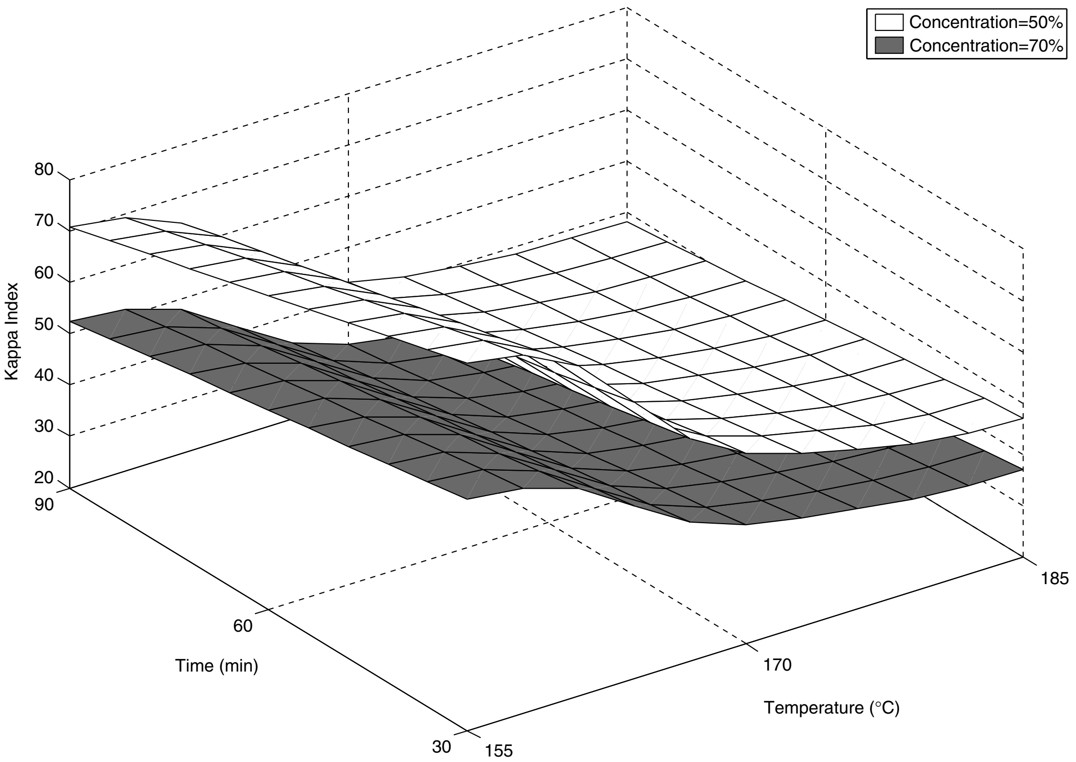

Fig. 4. Variation of kappa index with temperature and time at extreme ethanolamine concentrations.

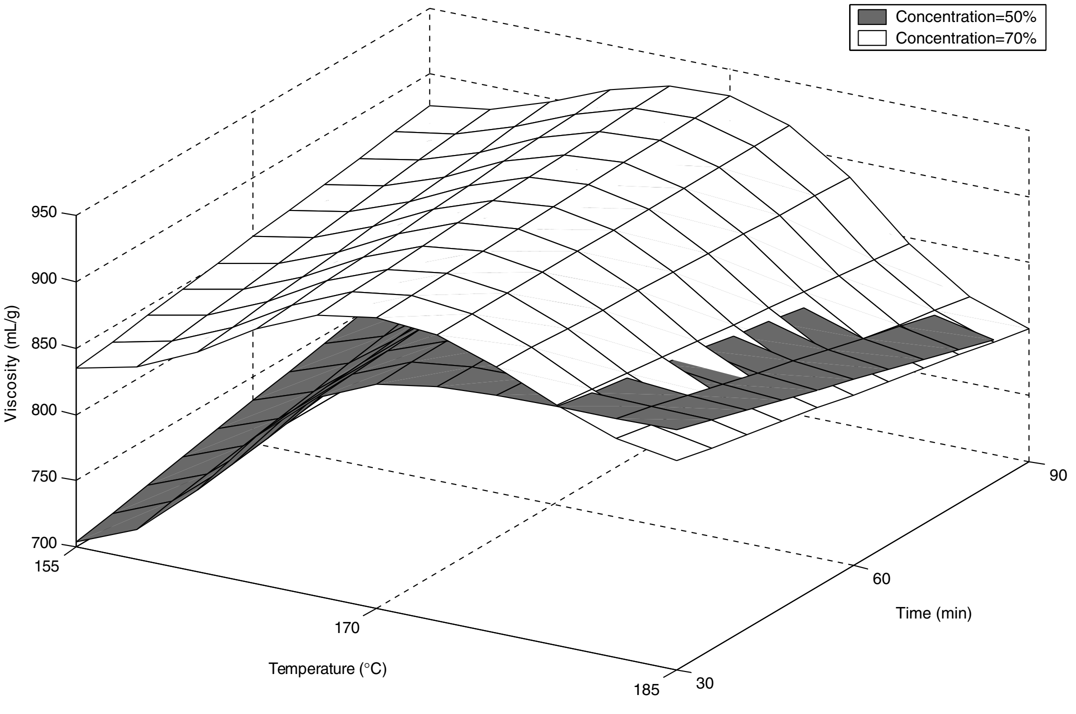

Fig. 5. Variation of viscosity with temperature and time at extreme ethanolamine concentrations.

capital on industrial facilities by using lower temperatures and shorter processing times. One combination leading to near-optimal properties with reduced costs is using a temperature of 180 °C and an ethanolamine concentration of 60% for 60 min, to obtain pulp with a viscosity of 6.13% lower than the maximum value (932.8 ml/g) and a drainability of 5.49% lower than the maximum value (71 °SR).

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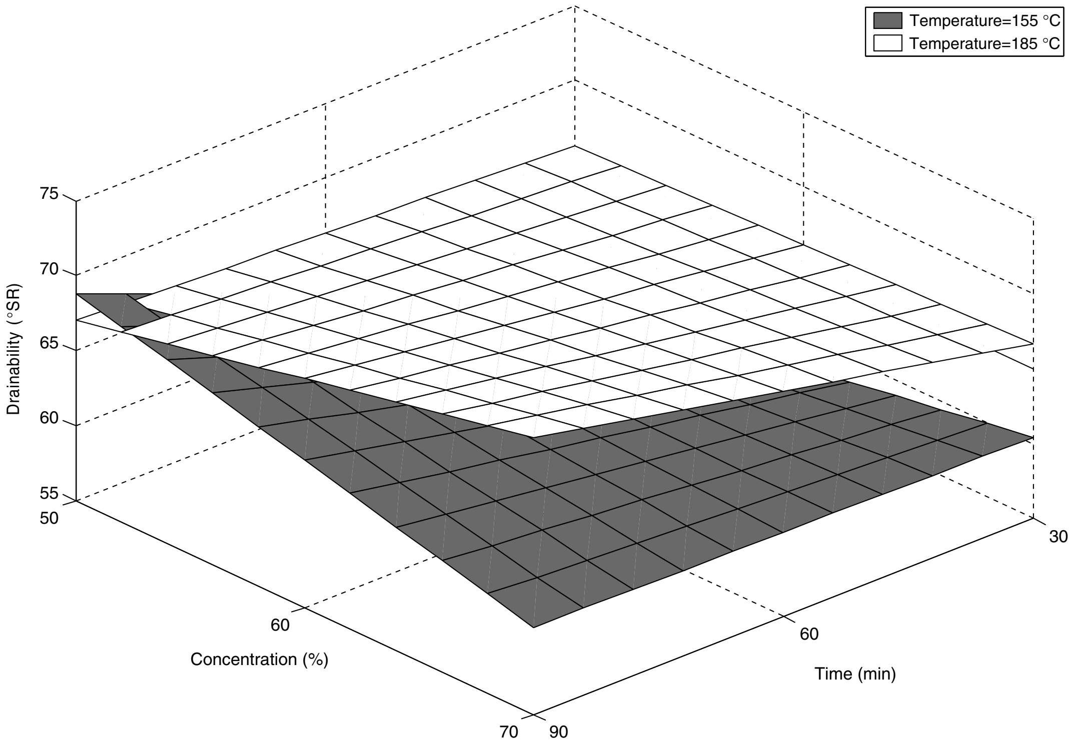

Fig. 6. Variation of drainability with time and ethanolamine concentration at extreme temperatures.

### 3.2. Neural fuzzy modelling

Table 5 shows the values of the neural fuzzy modelling constants, $c_i$, as obtained by using the drainability data of Table 1 with linear membership functions at two levels (low and high) for the three operational variables.

Table 5 lists the values of parameters $c_l$ in the neural fuzzy modelling equations for the pulp yield, kappa index and viscosity as obtained by using a Gaussian membership function at three levels (low, medium and high) for the variable temperature and a linear membership function at two levels (low and high) for the other two.

Table 6 gives the estimated values of the dependent variables as calculated with the models, as well as their deviations from the experimental values. As can be seen, the differences were all small, so the neural fuzzy modelling method provides accurate predictions for the pulping of vine shoots with ethanolamine.

The proposed models were validated by conducting three pulping experiments. The values of the operational variables and those of the properties of the resulting pulp are shown in Table 7 together with the calculated values of the dependent variables provided by the neural fuzzy models used and the errors in the predictions. As can be seen, the predicted values departed little from their experimental counterparts, which testifies to the accuracy of the neural fuzzy models used.

Figs. 3–6 show two selected response surfaces obtained at a high and low value of an operational variable as a function of the other two.

## 4. Conclusions

The results of this work allow us to draw the following conclusions:

(a) Based on the $p$, Student's $t$ and $R^2$ values obtained, the proposed polynomial and neural fuzzy models can be used to accurately predict pulp properties as a function of the operating conditions used.
(b) The neural fuzzy models used involve roughly the same number of parameters as second-order polynomial models. This allows simple neural fuzzy models to be employed with experiments involving only 15 tests – the typical number with polynomial models.
(c) Neural fuzzy models provide a physical interpretation of the constants (parameters) as these represent the average value of each property (dependent variable) under the conditions defined by the specific fuzzy rule. Thus, the average pulp yield obtained with a low temperature, time and ethanolamine concentration was 63.89%, which is almost identical with the parameter value in the equation. This provides an additional advantage over polynomial models.
(d) Neural fuzzy models allow one to assess the influence of each operational variable on pulp properties. Thus, at a low temperature and time, increasing the ethanolamine concentration would slightly lower the yield (from 63.89% to 52.50%) as per rules 1 and 2 in Table 4. Also, increasing the pulping time at a low temperature and concentration would decrease the pulp yield from 63.89% to 42.88% as

per rules 1 and 3. This allows one to compare any two rules involving identical levels of two variables and differing in the third in order to make reliable predictions by determining the influence of the third variable on each pulp property.

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# Hydrothermal treatment and ethanol pulping of sunflower stalks

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## Abstract

The influence of temperature in the hydrothermal treatment of sunflower stalks on the composition of the liquid fraction obtained was examined. The remaining solid fraction was subjected to ethanol pulping in order to obtain pulp that was used to produce paper sheets. The pulp was characterized in terms of yield, kappa index, viscosity, and cellulose, hemicellulose and lignin contents; and the paper sheets in terms of breaking length, stretch, burst index and tear index.

Hydrothermal treatment of the raw material at 190 °C provided a liquid phase with maximal hemicellulose-derived oligomers and monosaccharide (glucose, xylose and arabinose) contents (26.9 and 4.2 g/L, respectively).

Pulping the solid fraction obtained by hydrothermal treatment at 180 °C, with 70% ethanol at a liquid/solid ratio of 8:1 at 170 °C for 120 min provided pulp with properties on a par with those of soda pulp from the sunflower stalks, namely: 36.3% yield, 69.1% cellulose, 12.6% hemicellulose, 18.2% lignin and 551 ml/g viscosity. Also, paper sheets obtained from the ethanol pulp were similar in breaking length (3.8 km), stretch (1.23%), burst index (1.15 kN/g) and tear index (2.04 m $Nm^2$/g) to those provided by soda pulp.

*Keywords:* Sunflower stalks; Hydrothermal treatment; Ethanol pulping; Pulp; Paper

## 1. Introduction

The need to use the cellulose fraction of plant biomass to obtain cellulose pulp can result in the loss of other components of lignocellulosic materials. This makes it advisable to integrate byproduct manufacturing lines into cellulose pulp production lines in order to exploit the hemicellulose and lignin fractions of the raw materials (Ariza et al., 2005).

The use of lignocellulosic fractions in hardwood and softwood for various purposes has previously been assessed (Rijkens, 1984). However, lignocellulosic fractions in residual materials such as agricultural and agroindustrial residues are especially appealing in this respect on account of the ecological advantages gained by suppressing a source of pollution and valorizing the residues.

One way of fractionating such materials is by subjecting them to hydrothermal treatment with hot water in order to remove some substances that may introduce impurities in the cooked pulp and hinder delignification during the pulping process. In fact, hot water dissolves, and increases the solubility of, some substances, and causes autohydrolysis of polysaccharides (hemicelluloses mainly) to hemicellulose-derived oligomers and monosaccharides (xylose, glucose, arabinose). The sugars thus obtained can be used for various purposes (Vázquez et al., 2005; Vegas et al., 2004; Garrote et al., 2001; Carvalheiro et al., 2004) and the remaining residue, which consists mainly of cellulose, processed to obtain cellulose pulp (Ariza et al., 2005).

There is a growing trend to manufacture fine paper from short fibers rather than cut long fibers (Burley et al., 2004). Hardwood can give well-formed strong sheets, so much so that softwood and hardwood pulp produce paper of nearly identical quality (Baker, 1995). The use of non-wood, faster-growing species or agricultural residues to produce paper can be highly advantageous as a remedy for the environmental problems associated with the industrial use of such plant species.

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Sunflower stalks are a highly abundant agricultural residue in may areas. In Spain, they are produced in amounts exceeding 2 million ton each year (Jiménez et al., 1997). Like cereal straw, sunflower stalks can be easily collected and stored with available agricultural equipment. This has aroused much interest in their use as a raw material for paper pulp (Jiménez et al., 1991, 1993; Jiménez and López, 1993; Khristova et al., 1998; López et al., 2000, 2003, 2005).

This paper examines the influence of a hydrothermal pretreatment used to obtain a valuable liquid phase in addition to a solid fraction amenable to ethanol pulping. Pulp thus obtained was analysed for yield, kappa index, viscosity, and cellulose, hemicellulose and lignin contents; and paper sheets made from it were characterized in terms of breaking length, stretch, burst index and tear index.

## 2. Experimental

### 2.1. Raw material

Aliquots of raw material were ground to particle size <0.5 mm and subjected to moisture and extractives determination (TAPPI T-264-om-88) and to quantitative acid hydrolysis with 72% $H_2SO_4$ following standard methods (T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. Hydrolyzates were analyzed for monosaccharides (glucose coming from cellulose; xylose and arabinose coming from hemicelluloses) and acetic acid (coming from acetyl groups) by HPLC. Chromatographic determination was performed using an Agilent 1100 HPLC equipped with an ion-exchange resin Aminex HPX-87H column under the following conditions: mobile phase, 0.05 mol/L of sulfuric acid; flow rate, 0.6 ml/min; and column temperature, 40 °C.

### 2.2. Hydrothermal treatment

Sunflower stalk specimens were milled to pass through a 8 mm screen – particle size that was found to impose no diffusional restrictions in preliminary tests.

Milled sunflower stalks were mixed with water in the desired proportions, heated in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers at temperatures from 160 to 220 °C by means of external mantles for preset times and cooled. Once normal pressure was regained, the reactor was opened and samples of the resulting suspensions withdrawn. The solid/liquid ratio was fixed at 1/8 kg oven-dry raw material/kg water, which is the lowest level found to ensure homogenous mixing in practice.

After treatment, solid residues were recovered by filtration and washed with distilled water, a fraction being pulped and another air-dried and milled to a particle size less than 0.5 mm to determine α-cellulose (glucan), hemicellulose (xylan + araban + acetyl groups) and lignin, using the same methods as for the raw material.

The liquor was filtered through membranes of 0.45 µm pore size and used for direct HPLC determination of oligosaccharides, monosaccharides (glucose, xylose and arabinose), furfural, 5-hydroxymethylfurfural (HMF), and acetic and formic acids. With this type of column, xylose can be eluted together with mannose and galactose.

### 2.3. Pulping

Cellulose pulp was obtained in the same reactor used in the hydrothermal pretreatment. Cooking tests were performed under (a) mild (50% ethanol, 145 °C, 40 min) or (b) drastic conditions (70% ethanol, 175 °C, 120 min). The initial liquor-to-solid ratio was 8:1 (on a dry weight basis) in all tests. Following loading, the reactor was closed and simultaneously heated and actuated to ensure homogeneous mixing and uniform swelling of the solid residues from the hydrothermal treatment. Once the preset pulping time elapsed, the reactor was chilled to 25 °C. After cooking, the pulp was separated from the liquor and disintegrated without disturbing the fibers for 3 min, washed on a sieve of 0.16 mm mesh, defibered and passed through a Strainer filter of 0.4 mm mesh to isolate uncooked material. The ethanol concentration for washing, disintegrating and ethanol pulping are the same in all the experiments. The operation temperature was 50 °C.

### 2.4. Characterization of the pulp and paper sheets

Characterization experiments of pulps and raw materials involved the same parameters (see Section 2.1). In addition, the pulp was characterized in terms of yield (Tappi 257) and viscosity (Tappi 230).

The paper sheets obtained from the pulp were characterized for breaking length and stretch (UNE-57-055-79 and UNE-57-028), burst index (UNE-57-055-79 and UNE-57-058) and tear index (UNE-57-055-79 and UNE-57-033).

## 3. Results and discussion

### 3.1. Composition of raw material

The sunflower stalks used had the following composition (average of four replicates; values in g/100 g raw material, on dry basis, standard deviation in braquets):

Glucan: 33.8 (0.26); xylan: 23.9 (0.26); araban: 0.37 (0.00); acetyl groups: 4.32 (0.10) and lignin: 19.9 (0.17).

### 3.2. Hydrothermal treatment

Table 1 shows the proportion of material dissolved by the hydrothermal treatment. As can be seen, it increased with increasing temperature up to 26.1% at 190 °C, beyond which in started to decrease.

Table 2 lists the concentrations of sugars and other components of the liquid phase provided by the hydrothermal treatment. As can be seen, the total amount of sugars increased with increasing operating temperature, with a peak of 26.9 g/L for hemicellulose-derived oligomers and

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Table 1
Fractions dissolved by the hydrothermal treatment of sunflower stalks (percent weights relative to the amount of raw material)

| Temperature (°C) | Unsolubilized fraction (%)[a] | Solubilized fraction (%) |
|---|---|---|
| 160 | 85.7 | 14.0 |
| 165 | 84.1 | 15.2 |
| 170 | 81.1 | 18.7 |
| 175 | 80.3 | 19.5 |
| 180 | 78.4 | 20.9 |
| 190 | 73.7 | 26.1 |
| 200 | 72.5 | 24.5 |

[a] Solid residue yield (g of solid residue recovered after hydrothermal treatment/100 g raw material, o.d.b.)

Table 2
Concentration of components derived from the hemicellulose fraction of sunflower stalks by the hydrothermal treatment

| Temperature (°C) | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|
| Hemicellulose-derived oligomers (g/L) | 9.5 | 11.3 | 13.6 | 21.0 | 24.2 | 26.9 | 23.3 |
| Glucose (g/L) | 0.5 | 0.6 | 1.2 | 0.8 | 1.2 | 1.0 | 0.7 |
| Xylose (g/L) | 1.3 | 1.6 | 1.7 | 2.0 | 1.9 | 2.6 | 2.1 |
| Arabinose (g/L) | 0.0 | 0.1 | 0.2 | 0.3 | 0.5 | 0.6 | 0.6 |
| Formic acid (g/L) | 0.2 | 0.3 | 0.3 | 0.4 | 0.8 | 0.8 | 1.0 |
| Acetic acid (g/L) | 0.4 | 0.5 | 1.0 | 1.1 | 2.4 | 2.4 | 4.6 |
| HMF (g/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Furfural (g/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |

one of 4.2 g/L for monosaccharides (glucose, xylose and arabinose) at 190 °C. Also, monosaccharides were present in much smaller amounts than hemicellulose-derived oligomers, and so were acetic acid (from the attack of protons on acetyl groups) and other degradation products formed in hydrolysis-related side reactions.

Table 3 shows the yields of hemicellulosic sugars in the liquid phase provided by the hydrothermal treatment. The results confirm the high efficiency of the treatment in extracting hemicellulose-derived oligomers from sunflower stalks at temperatures above 180 °C. The maximum concentration extracted (at 190 °C) was 21.5 g of hemicellulose-derived oligomers per 100 g of raw material.

In order to minimize degradation of the solid phase while maximizing xylan removal, we chose to use 180 °C for the hydrothermal treatment, and the subsequent pulping of the resulting solid phase. These conditions would also result in less marked fiber degradation than a high temperature such as 190 or 200 °C, where Heitz et al. (1991) found a diminution of the degree of polymerization of cellulose, and Garrote et al. (2002) found extensive decrease of cellulose fibers through autohydrolysis.

Table 3
Recovery of hemicellulosic sugars (g sugar/100 g material) in the liquid phase provided by the hydrothermal treatment of sunflower stalks

| Temperature (°C) | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|
| Hemicellulose-derived oligomers | 7.60 | 9.03 | 10.87 | 16.79 | 19.35 | 21.51 | 18.63 |
| Glucose | 0.40 | 0.48 | 0.96 | 0.64 | 0.96 | 0.80 | 0.56 |
| Xylose | 1.04 | 1.28 | 1.36 | 1.60 | 1.52 | 2.08 | 1.68 |
| Arabinose | 0.00 | 0.08 | 0.16 | 0.24 | 0.40 | 0.48 | 0.48 |

Table 4
Composition of the raw material and of the solid residue provided by the hydrothermal treatment

| Component | Sunflower stalks | Solid fraction by hydro-thermal treatment |
|---|---|---|
| Glucan | 33.8 | 43.4 |
| Xylan | 23.9 | 12.9 |
| Araban | 0.37 | 0.05 |
| Acetyl groups | 4.3 | 3.10 |
| Lignin | 19.9 | 25.5 |

Table 5
Properties of the pulp and paper sheets obtained by ethanol pulping of the solid fraction provided by the hydrothermal treatment of sunflower stalks

| Parameter | Operational conditions: Temperature (°C), time pulping (min) and ethanol concentration (%) | |
|---|---|---|
| | Conditions a: | Conditions b: |
| | 145, 40 y 50 | 175, 120 y 70 |
| Yield, % | 52.0 | 36.3 |
| Cellulose, % | 56.0 | 69.1 |
| Hemicellulose, % | 13.2 | 12.6 |
| Lignin, % | 19.5 | 18.2 |
| Viscosity, ml/g | 353 | 551 |
| Breaking length, km | 2.38 | 3.81 |
| Stretch, % | 1.09 | 1.23 |
| Burst index, kN/g | 0.97 | 1.15 |
| Tear index, m Nm$^2$/g | 1.29 | 2.04 |

Table 4 shows the composition of the solid residue provided by the hydrothermal treatment at 180 °C and that of the raw material. As can be seen, the treatment increased the glucan content as the cellulose fraction underwent no significant degradation. Also, it increased the proportion of lignin in the residue. On the other hand, the treatment reduced the amount of hemicellulose through hydrolysis.

### 3.3. Pulping

Table 5 shows the results obtained in the pulping of the solid fraction provided by the hydrothermal treatment at 180 °C under the mild and drastic conditions described in the Experimental section (a and b). As can be seen, the drastic conditions (b) reduced the yield and the hemicellulose and lignin contents, but increased the viscosity and cellulose content of the pulp, and improved the physical properties of the paper sheets, relative to the mild conditions (*a*).

Garrote et al. (2003) applied an identical treatment to eucalyptus wood and obtained the following maximum values: 3.2 km breaking length, 0.87 kN/g burst index and 1.11 m Nm$^2$/g tear index – all of which are slightly smaller than those obtained our sunflower stalks. Jiménez et al. (2004) obtained ethanol-water pulp from untreated wheat

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Table 6
Results obtained by several authors in the soda pulping of sunflower stalks

| Conditions of puling of sunflower stalks | Yield, % | Cellulose, % | Lignin, % | Breaking length, m | Stretch, % | Burst index, kN/g | Tear index, m Nm$^2$/g |
|---|---|---|---|---|---|---|---|
| 11,85% soda, 147 °C, 60 min, 6:1 liquid/solid (Jiménez et al., 1991, 1993) | 53.7 | 56.0 | 23.0 | 3.85 | 1.48 | 1.46 | 5.11 |
| 12,16% soda, 147 °C, 60 min, 6:1 liquid/solid (Jiménez and López, 1993) | 47.9 | 59.0 | 20.0 | 5.49 | 1.29 | 1.62 | 5.55 |
| 5,00% soda, 125 °C, 30 min, 6:1 liquid/solid (López et al., 2003) | 66.9 | – | – | 2.76 | 1.21 | 1.34 | 4.72 |
| 18% soda, 170 °C, 90 min, 5:1 liquid/solid (Khristova et al., 1998) | 36.3 | – | – | 4.05 | – | 2.89 | 6.00 |
| 16% soda, 0,13% anthraquinone, 170 °C, 90 min, 5:1 liquid/solid (Khristova et al., 1998) | 38.4 | – | – | 4.22 | – | 3.39 | 3.67 |
| 15% soda, 0,1% anthraquinone, 170, °C, 90 min, 6:1 liquid/solid (Khristova et al., 1998) | 43.5 | – | – | 7.69 | – | 3.60 | 3.96 |
| 13.9% soda, 0,1% anthraquinone, 175 °C, 30 min, 4:1 liquid/solid (López et al., 2005) | 40.6 | – | 21.4 | 2.72 | – | 1.00 | 4.10 |

straw that provided paper sheets with physical properties roughly similar to those of the sheets obtained in this work.

A comparison of the properties of the pulp and paper sheets obtained from the solid fraction provided by the hydrothermal treatment of sunflower stalks (Table 5) with those previously obtained by some authors (Jiménez et al., 1991, 1993; Jiménez and López, 1993; Khristova et al., 1998; López et al., 2003, 2005) from untreated sunflower stalks (Table 6) reveals that applying drastic pulping conditions [(b) 70% ethanol, 175 °C and 120 min] to hydrothermally pretreated sunflower stalks provides low yield and tear index values relative to soda pulp from untreated stalks. Khristova et al. (1998) used a high soda concentration (18%) and obtained a yield similar to ours. On the other hand, the hydrothermal treatment resulted in an increased proportion of cellulose and a decreased amount of lignin in the pulp. Finally, the breaking length, stretch and burst index for our paper sheets were somewhat smaller than previously reported values – some, however, correspond to refined rather than crude pulp.

Based on the foregoing, traditional (soda) cooking provides pulp with slightly better properties than organosolv pulp; however, organosolv processes are environmentally advantageous as they allow the pulping solvent to be easily recovered and various byproducts such as lignin to be obtained. Also, a hydrothermal pretreatment of sunflower stalks enables the conversion of hemicelluloses into useful sugars for various purposes.

In summary, the proposed procedure is an effective, environmentally benign choice for the pulping of sunflower stalks and their valorization as a raw material for the joint production of oligosaccharides and paper pulp.

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# Autohydrolysis of *Arundo donax* L., a Kinetic Assessment

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*Arundo donax* L. was submitted to a process of isothermal autohydrolysis in the temperature range of 150−195 °C, for periods between 0 and 15 h and a liquid/solid ratio = 8 g g$^{-1}$, for the purpose of hydrolyzing the hemicelluloses to oligomers (compounds which are of interest to the food industry) and monomers. A conventional kinetic model was developed that explains the evolution over time of the hemicelluloses and hemicellulose degradation products. Kinetic modeling was also carried out using the severity factor approach and the kinetic parameters obtained in these two ways have been compared.

## 1. Introduction

Considered as raw materials, lignocellulosic materials (LCM) display certain advantages, such as their abundance, their renewable character, and their low cost, which make them suitable for use as a raw material in various industries. These materials are made up fundamentally of cellulose (a linear polymer of glucose units), hemicelluloses (a ramified polymer made up of different monomers such as arabinose, glucose, galactose, manose, or xylose and substituents such as the acetyl groups or the uronic acids), and lignin (a three-dimensional polymer formed by units of phenylpropane), together with other minority fractions (such as extracts or ash). In the case of hardwoods and agricultural materials, the majority hemicellulosic fraction is called xylan, formed by a structure of monomers of xylose with different ramifications such as arabinose, acetyl groups, or uronic acids.[1]

The most important use of LCMs in the chemical industry is in the production of cellulose pulp, using technologies that make use of only one of the fractions, cellulose, while the rest of the fractions are discarded or used for the generation of energy. A more efficient approach is to use sequential processes of fractioning, which make it possible to obtain the main fractions of LCMs in differentiated streams, allowing for an individualized exploitation of each, maximizing benefits and reducing byproducts; this is the “biomass refinery” philosophy.[2]

The first step in this fractionation can be the solubilization of the hemicelluloses through autohydrolysis processes. In these processes, an aqueous suspension of LCM is subjected to heating; the hydronium ions (resulting in the first instance from the ionization of the water and then from the hydrolysis of the acetyl groups or the uronic acids present in the raw materials) catalyze the depolymerization of the hemicelluloses passing to the liquid phase as a mixture of oligosaccharides, monosaccharides, and other products such as acetic acid, furfural, or hydroxymethylfurfural (HMF). The solid phase of these treatments is fundamentally made of lignin and cellulose and can be subsequently fractioned and allocated to applications with high added value. Compared with other solubilization treatments of hemicelluloses such as prehydrolysis or acid hydrolysis, autohydrolysis has advantages such as the following:[3] There are no problems of corrosion or problems related to the handling of the neutralization residues for the acids used in acid hydrolysis. Cellulose is not solubilized since gentle operating conditions are maintained. The production of sugar degradation compounds is minimized. The solid residue offers greater susceptibility for subsequent phases of fractioning, such as the enzymatic hydrolysis of cellulose (since, although this is not solubilized, its structure is altered)[4−7] or delignification (owing to the partial degradation of the lignin).[8−11.]

When autohydrolysis is performed on materials that are rich in xylan, a liquid phase rich in xylooligosaccharides may be obtained. These compounds can be used in the pharmaceutical industry, in the production of animal foods, and in the food industry. As ingredients of functional foods, they possess prebiotic action and increase the amount of Bifidobacteria.[12−17]

An interesting raw material for its hydrothermal processing is *Arundo donax* L. (common name “giant reed”), which is a perennial grass that grows quickly, adapts easily to different habitats, and exhibits very high levels of productivity (on the order of 10−75 t hectare$^{-1}$).[18,19]

Kinetic modeling can be conducted using two strategies: the use of severity factors or formal kinetic models. Severity factors utilize approximations that make it possible to predict in a simple fashion the kinetics of simple irreversible reactions, such as the solubilization of hemicelluloses, but they are not applicable to more complex cases of reactions in series, such as those that take place in hydrothermal processes. Formal kinetics are based on the formulation of conventional kinetic models, normally through the use of pseudo-homogeneous, first-order, irreversible reactions, that allow us to obtain a more complete description of the process (solubilization of hemicelluloses, formation and rupture of oligomers, formation of xylose, etc.), but these are more complex to formulate.

Developing kinetic models displays certains advantages such as the following:

(1) A better comprehension of the autohydrolysis process is allowed in order to provide information about hemicellulose solubilization, the solubilization rate of the several fractions, etc. This is valuable information to predict in a quantitative way the evolution of an autohydrolysis process. If kinetic models are not available, it is necessary to carry out an experiment for every operation condition and achieving conclusions is more difficult.

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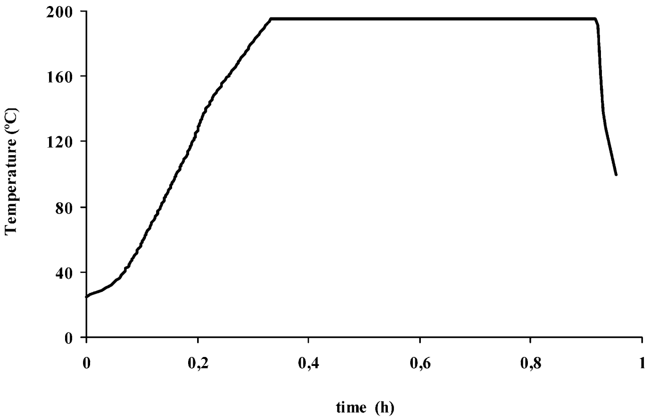

**Figure 1.** Temperature profile employed in this work (example for 195 °C).

(2) They provide mathematical equations which describe the time−temperature course of the different compounds, and those equations can be used for tecnoeconomic optimization studies.

The obtained models are suitable to be used with other lignocellulosic substrates. Initial concentrations and the values of kinetic parameters would be different. This is specially true with similar lignocellulosic materials (agricultural materials and hardwoods) whose hemicelluloses are of a similar composition (fundamentally araban and xylan). In the case of softwoods, a deep adaptation of the model would be necessary since the chemical composition of their hemicelluloses is radically different.

This work is about the study of the kinetics of solubilization of hemicelluloses during the autohydrolysis of *Arundo donax* L. For the purpose of studying the production of **xylooligosaccharides** with high yields from Arundo, a series of hydrothermal treatments were carried out. The key operational variables (temperature and reaction time) were varied in the ranges 150−195 °C and 0−15 h, respectively. In this work, both strategies of kinetic modeling (severity factors and formal kinetic models) are studied and compared.

## 2. Materials and Methods

**2.1. Raw Material.** *Arundo donax* L. samples from local plantations were milled to pass a 8 mm screen, since in preliminary studies no diffusional limitations were observed for this particle size. Samples were air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored.

**2.2. Analysis of Raw Material.** Aliquots of raw material were ground to a particle size < 0.5 mm and subjected to moisture and extractives determination (TAPPI T-264-om-88) and to quantitative acid hydrolysis with 72% $H_2SO_4$ following standard methods (T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. The monosaccharides (glucose, xylose, and arabinose) and acetic acid contained in the hydrolysates were determined by high-performance liquid chromatography (HPLC), as reported elsewhere.[20] Uronic acids were determined spectrophotometrically[21] using galacturonic acid as a standard for quantification. Ashes were determined by calcination (T-244-om-93).

**2.3. Hydrothermal Processing of *Arundo donax* Samples.** Raw material and water were mixed in the desired proportions and treated in a 600 cm$^3$ stainless steel reactor (Parr Instruments Company, Moline, IL) using a liquid/solid ratio of 8 kg water kg raw material$^{-1}$, on a dry basis (the moisture content of the material was considered to be water). Previous works demonstrated that the influence of the variation of the liquid/solid ratio is practically negligible.[20,22] The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle, and cooled by cool water circulating through an internal loop. The reaction media was stirred at 150 rpm and heated for 14−20 min to reach the desired temperature following the temperature profile show in Figure 1. Since a portion of the substrate has reacted during the period of heating, data corresponding to the isothermal part of the reaction were used for kinetic modeling. Time zero was considered to be the beginning of the isothermal stage. A total of 40 experiments were carried out at temperatures of 150, 165, 180, and 195 °C (9−11 experiments for each temperature). Triplicates of zero-time experiments have been carried out (data not show), so differences lower than 2% have been always found; subsequently, it could be considered that there are not significant variations caused by the heating profile.

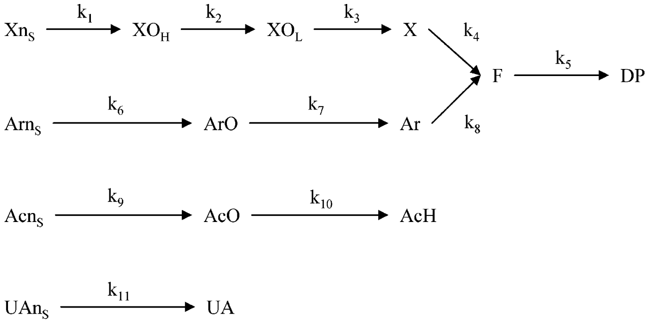

**Figure 2.** Kinetic model for the autohydrolysis of *Arundo donax* (see text for variable definitions).

**Table 1. Optimal Values of $\alpha_X$, $\alpha_{Ar}$, $\alpha_{AG}$, $\alpha_U$, $k_1-k_{11}$, and $R^2$ for the Autohydrolysis of *Arundo donax***

| | temperature (°C) | | | |
|---|---|---|---|---|
| | 150 | 165 | 180 | 195 |
| $\alpha_X$ (dimless) | 0.808 | 0.808 | 0.808 | 0.808 |
| $\alpha_{Ar}$ (dimless) | 0.940 | 0.940 | 0.940 | 0.940 |
| $\alpha_{AG}$ (dimless) | 0.912 | 0.912 | 0.912 | 0.912 |
| $\alpha_U$ (dimless) | 0.903 | 0.903 | 0.903 | 0.903 |
| $k_1$ (h$^{-1}$) | 0.124 | 0.515 | 1.593 | 7.791 |
| $k_2$ (h$^{-1}$) | 0.230 | 0.744 | 1.881 | 5.009 |
| $k_3$ (h$^{-1}$) | 0.230 | 0.744 | 1.881 | 5.010 |
| $k_4$ (h$^{-1}$) | 0.101 | 0.420 | 0.848 | 2.609 |
| $k_5$ (h$^{-1}$) | 0.808 | 2.135 | 4.260 | 13.61 |
| $k_6$ (h$^{-1}$) | 0.321 | 1.027 | 3.570 | 12.68 |
| $k_7$ (h$^{-1}$) | 0.236 | 1.093 | 3.236 | 9.221 |
| $k_8$ (h$^{-1}$) | 0.109 | 0.299 | 0.981 | 4.655 |
| $k_9$ (h$^{-1}$) | 0.151 | 0.587 | 1.920 | 6.432 |
| $k_{10}$ (h$^{-1}$) | 0.380 | 0.974 | 1.289 | 3.850 |
| $k_{11}$ (h$^{-1}$) | 0.175 | 0.603 | 1.883 | 8.654 |
| $R^2$ for Xn | 0.983 | 0.997 | 0.994 | 0.988 |
| $R^2$ for XO | 0.938 | 0.983 | 0.967 | 0.942 |
| $R^2$ for X | 0.960 | 0.995 | 0.967 | 0.942 |
| $R^2$ for Arn | 0.992 | 0.991 | 0.993 | 0.988 |
| $R^2$ for ArO | 0.947 | 0.815 | 0.875 | 0.759 |
| $R^2$ for Ar | 0.931 | 0.950 | 0.918 | < 0.7 |
| $R^2$ for F | 0.970 | 0.999 | 0.984 | 0.956 |
| $R^2$ for Acn | 0.997 | 0.998 | 0.998 | 0.995 |
| $R^2$ for AcO | 0.994 | 0.995 | 0.988 | 0.969 |
| $R^2$ for UAn | 0.998 | 0.996 | 0.985 | 0.970 |

The final time (0.4−15 h) was selected in order to allow a complete observation of the course of the hydrothermal process.

The temperature control has been carried out using a 4842 digital control module with standard parameters defined by the ParrInst company. When an experiment reaches its temperature, it does not vary more than ±1 °C and it is stabilized less than 1 min later. An experiment where these rules were not carried out is not considered to develop the kinetic models.

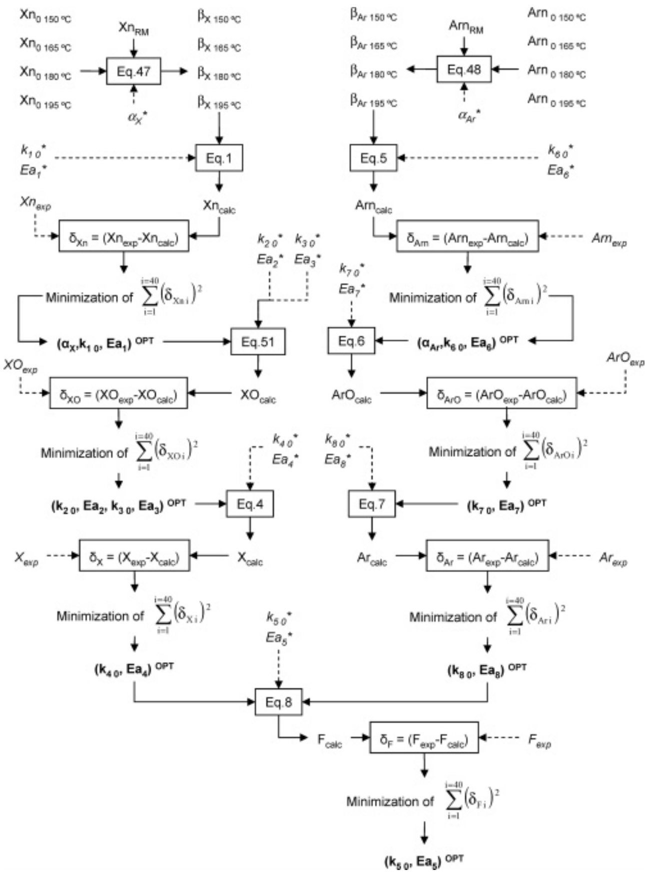

**Figure 3.** Calculation scheme developed for the determination of the optimal values of kinetic parameters using a generalized procedure.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, and weighted for yield determination. Aliquots of the solid residues were assayed for moisture and composition (duplicate) using the same methods as for raw material analysis. An aliquot of the liquors was oven-dried to a constant weight to determine the content in nonvolatile solids (duplicate, error < 0.5%). A second aliquot was filtered through 0.45 mm membranes and used for direct HPLC determination of monosaccharides, furfural, hydroxymethylfurfural, and acetic acid. A third aliquot was subjected to quantitative posthydrolysis (duplicate, error < 2%) with 4% $H_2SO_4$ at 121 °C for 45 min, before 0.45 mm membrane filtration and HPLC analysis. The increase in monosaccharide and acetic acid concentration caused by posthydrolysis provided a measure of the oligomer concentration. HPLC analyses were performed using a BioRad Aminex HPX-87H column at 30 °C eluted with 0.01 M $H_2SO_4$ at a flow rate of 0.6 mL·min$^{-1}$ using a refractive index detector to quantify glucose, xylose, arabinose, acetic acid, HMF, and furfural.

**2.5. Fitting of Data.** The experimental data were fitted to the proposed kinetic models by minimization of the sum of squares using commercial software with a built-in optimization routine based on Newton's method (Solver, Microsoft Excel). The data of the experimental and calculated values are shown in Figures 4−8.

**Table 2. Pre-exponential Factors ($k_{0i}$), Activation Energies ($E_{ai}$), and $R^2$ for Fitting the Kinetics Coefficients Listed in Table 2 to Arrhenius' Equation**

| | ln $k_0i$ ($k_0i$ in h−1) | $E_ai$ (kJ mol$^{-1}$) | $R^2$ | | ln $k_0i$ ($k_0i$ in h−1) | $E_ai$ (kJ mol$^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|---|
| $K_1$ | 40.1 | 149 | 0.994 | $k_7$ | 36.4 | 133 | 0.995 |
| $k_2$ | 30.3 | 112 | 0.999 | $k_8$ | 36.3 | 136 | 0.983 |
| $k_3$ | 30.3 | 112 | 0.999 | $k_9$ | 37.4 | 138 | 0.999 |
| $k_4$ | 30.5 | 115 | 0.987 | $k_{10}$ | 21.5 | 79.1 | 0.955 |
| $k_5$ | 28.3 | 100 | 0.988 | $k_{11}$ | 38.1 | 141 | 0.992 |
| $k_6$ | 37.1 | 135 | 0.998 | | | | |

**Table 3. Optimal Values of Susceptible Fractions ($\alpha_X$, $\alpha_{Ar}$, $\alpha_{AG}$, $\alpha_U$), Preexponential Factors ($k_{0i}$), Activation Energies ($E_{ai}$), and $R^2$ for the Autohydrolysis of *Arundo donax***

(a) Susceptible Fractions (dimensionless)

| $\alpha_X$ | $\alpha_{Ar}$ | $\alpha_{AG}$ | $\alpha_U$ |
|---|---|---|---|
| 0.802 | 1.000 | 0.912 | 0.893 |

(b) Pre-exponential Factors ($k_{0i}$) and Activation Energies ($E_{ai}$)

| | ln $k_{0i}$ ($k_{0i}$ in h$^{-1}$) | $E_{ai}$ (kJ mol$^{-1}$) |
|---|---|---|
| $k_1$ | 40.1 | 149 |
| $k_2$ | 30.4 | 112 |
| $k_3$ | 30.4 | 112 |
| $k_4$ | 31.7 | 119 |
| $k_5$ | 33.5 | 120 |
| $k_6$ | 36.8 | 134 |
| $k_7$ | 36.3 | 132 |
| $k_8$ | 36.5 | 137 |
| $k_9$ | 36.9 | 136 |
| $k_{10}$ | 20.9 | 76.7 |
| $k_{11}$ | 38.1 | 140 |

(c) Values of Statistical Parameter $R^2$

| | temperature (°C) | | | |
|---|---|---|---|---|
| | 150 | 165 | 180 | 195 |
| $R^2$ for Xn | 0.981 | 0.990 | 0.945 | 0.954 |
| $R^2$ for XO | 0.919 | 0.968 | 0.874 | 0.868 |
| $R^2$ for X | 0.958 | 0.977 | 0.942 | 0.844 |
| $R^2$ for Arn | 0.984 | 0.987 | 0.981 | 0.983 |
| $R^2$ for ArO | 0.908 | 0.742 | 0.921 | 0.671 |
| $R^2$ for Ar | 0.921 | 0.894 | 0.844 | $<0.7$ |
| $R^2$ for F | 0.961 | 0.993 | 0.963 | 0.946 |
| $R^2$ for Acn | 0.997 | 0.990 | 0.997 | 0.994 |
| $R^2$ for AcO | 0.994 | 0.990 | 0.959 | 0.954 |
| $R^2$ for UAn | 0.992 | 0.994 | 0.953 | 0.945 |

## 3. Results and Discussion

**3.1. Raw Material Composition.** The raw material composition is (average values of four replicates, data in weight percent, on a dry basis, standard deviations are shown within parenthesis) the following: glucan 35.15 (0.11); xylan 18.24 (0.04); araban 0.84 (0.03); acetyl groups 3.84 (0.34); uronic acids 5.53 (0.04); klason lignin 23.02 (0.13); extractives 9.11 (0.46); and ashes 3.06 (0.15). The majority fraction is cellulose (analyzed as glucan), at 35.15%, followed by the hemicelluloses (calculated as the sum of xylan, araban, acetyl groups, and uronic acids) at 28.45% and Klason's lignin at 23.02%. This composition is similar to that found by other authors for this material,[23−25] comparable to hardwoods, such as *Eucalyptus globulus*,[20] and other raw materials, such as *Bambusa procera acher*, *Cannabis sativa* L., *Cynara cardunculus* L., *Hisbicus cannabinus*, *Miscanthus sinensis*, *Saccharum officinarum*, *Sorgum bicolor*, etc.[26] Differences are found for the minority fractions, such as ash at 3.06%, and especially the ethanol-extractable content at 9.11%, which are suitable for use in obtaining antioxidant substances[27] or alkaloids.[28] With regard to hemicelluloses, the principal fraction affected by hydrothermal treatments, the molar relation between the different monomers, can be calculated.

$$\text{Xylose:Arabinose:Acetyl groups:Uronic acids} = 10{:}0.5{:}6.5{:}2.1$$

In which, it is observed that the predominant monomer is xylose, with a high degree of substitution with acetyl groups (up to 6.5

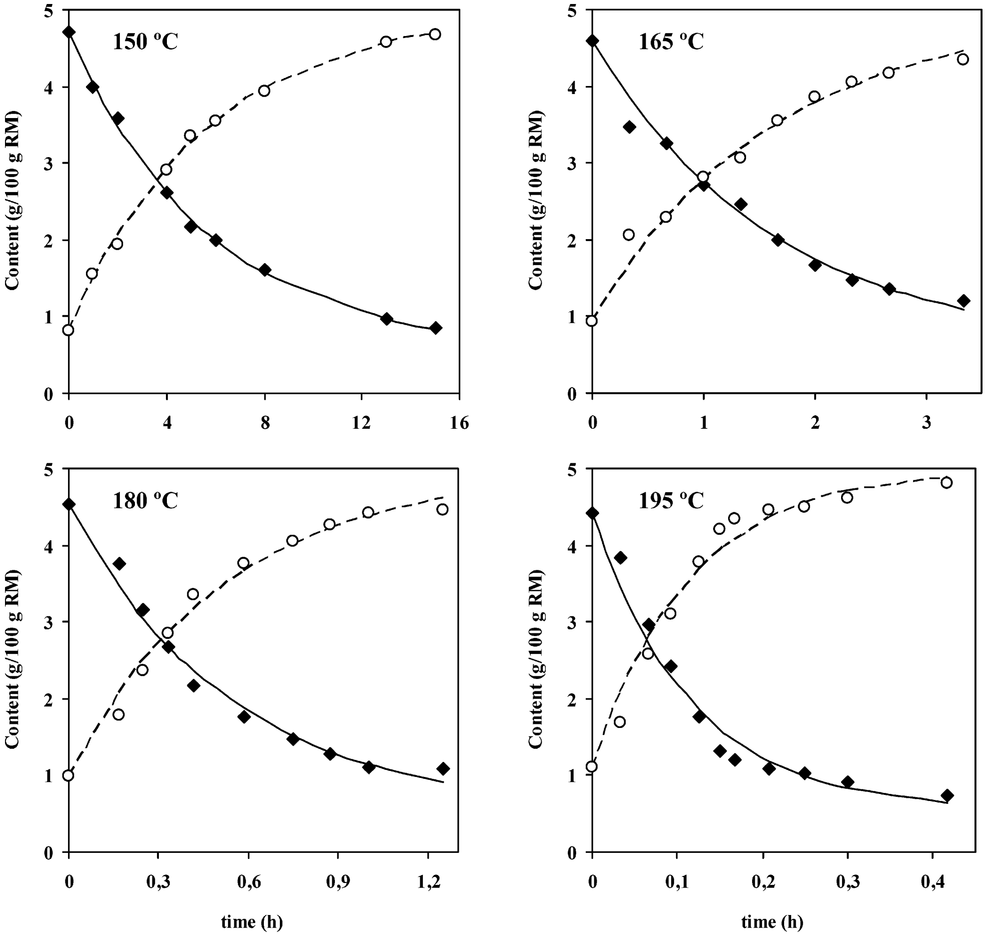

**Figure 4.** Experimental (symbols) and calculated (lines) time courses of uronic acids remaining in the solid phase (UAn: ◆, —) and uronic acids (UA: ○, - - - -).

acetyl groups for each 10 monomers of xylose) and to a lesser degree with substitutes such as arabinose and uronic acids. This composition is typical of acetylglucuronoxylans, which are typically present in hardwoods.

**3.2. Kinetic Model Using Pseudo-homogeneous Reactions.** The mechanism that is actually operating in hemicelluloses autohydrolysis is very complex and is not known in its entirety. The use of pseudo-homogeneous kinetics makes it possible to overcome the problem of the heterogeneity of the reaction medium and to consider that they take place in the liquid phase. A second difficulty is that hemicelluloses have a complex composition and a ramified structure. It should be emphasized that the formation and degradation of oligomers is much more complex than the way it is usually modeled; these substances may form oligomers of varying length, structure, and composition, which can in turn break down into other oligomers or into mixtures of oligomers and some monomers. In the case of the autohydrolysis of *Eucalyptus globulus*, conducted by our research group using the same apparatus and procedures, they were able to detect a great number of different oligomers.[29]

In light of these problems, it is appropriate for a kinetic model to be as simple as possible to enable it to explain in a satisfactory way the overall process of autohydrolysis, in view of which the following factors are taken into consideration:

**1. Hemicellulose Composition.** Hemicelluloses are considered to be composed of four species: xylose, arabinose, acetic acid, and uronic acid. Most kinetic models only take into account the xylose fraction (generically referred to as *xylan*), since it is the most abundant and characteristic of all hemicelluloses. Maloney[30] studied the acid hydrolysis of xylan and of the acetyl groups. More recently, kinetic models have been developed that take into account the existence of different fractions in the hemicelluloses and their interaction.[31−33]

**2. Hemicellulose Solubilization.** Practically all kinetic models of hemicellulose autohydrolysis or acid hydrolysis take into account the existence of two fractions within them, with different susceptibilities to hydrolysis. The difference with respect to the different speed of hydrolysis is usually attributed to differences in their composition or interphase transport limitations.[30,34,35] In autohydrolysis, the approach whereby a majority fraction is susceptible to solubilization while the other does not react under the conditions of the experiment has been successfully applied;[20,22,31] this hypothesis adequately fits with the experimental data, simplifies the kinetic model, and reduces the number of variables to be calculated without any resulting loss of precision, and therefore, this approach has been chosen.

**3. Formation and Degradation of Oligomers.** It is very complicated to formulate a model that rigorously explains the process of formation and degradation of oligomers and does not have a special practical utility when kinetics are used for process design or calculation of concentrations, which is why one should attempt the most simple approach that adequately fits the experimental data. The simplest approach is to use a single fraction of oligomers, but this approach is not suitable, as Conner and Lorenz already demonstrated in 1986,[36] since it does not predict the evolution of the concentration of oligomers and is rarely used. Various approaches have been successfully utilized: using depolymerization models;[37] using a kinetic constant for the degradation of oligomers that varies over time;[31,36] or taking into account two fractions within the

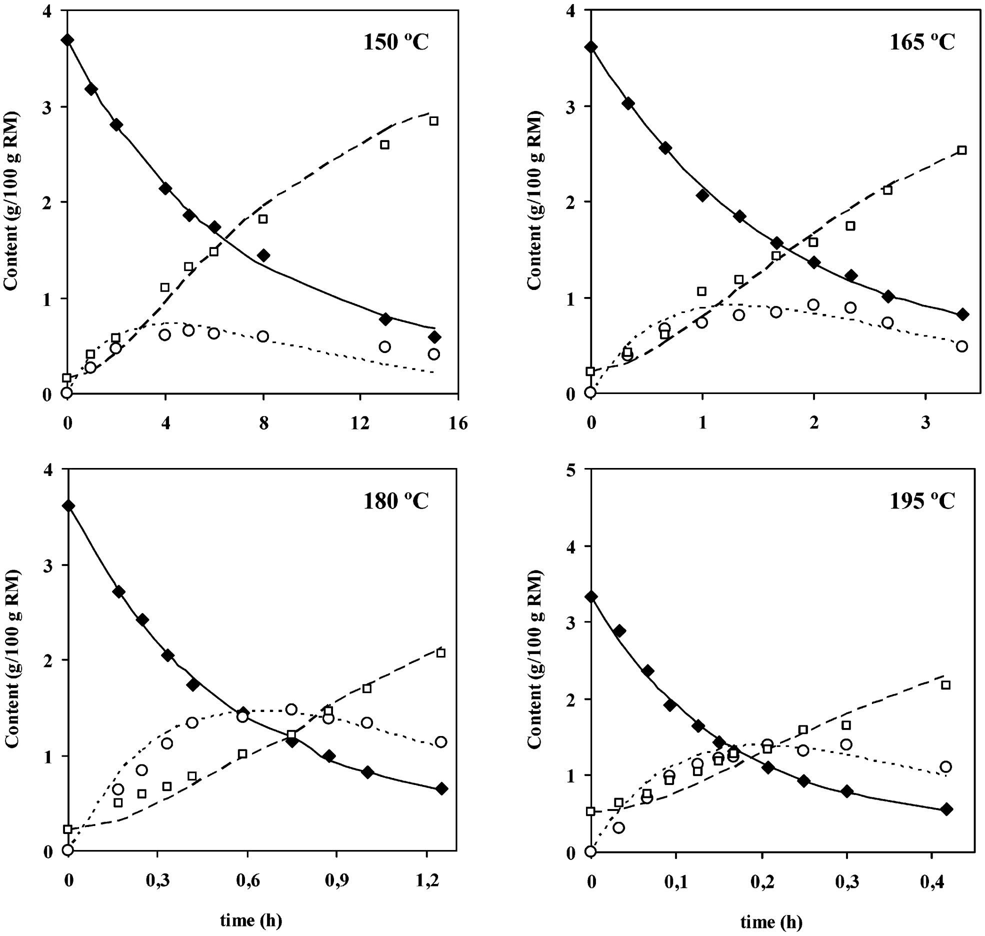

**Figure 5.** Experimental (symbols) and calculated (lines) time courses of acetyl groups remaining in the solid phase (Acn: ◆, —), acetyl groups linked to oligomers (AcO: ○, - - - -), and acetic acid (AcH: □, — — —).

oligomers, high molecular weight oligomers and low molecular weight oligomers.[20,30,31] The two last approaches involve using a single additional kinetic parameter.

**4. Formation and Degradation of Monomers.** Consider the degradation of xylose and arabinose to furfural. Given that both monomers can generate furfural, this has been taken into account in the kinetic model. No experimental evidence has been found of the degradation of acetic acid or uronic acids.

**5. Other Products of Decomposition.** Achieving material balances for arabinose and xylose, it is observed that with long reaction times the sum of fractions measured is less than the content of the raw material, which is why the decomposition reaction of furfural has been taken into account. Decomposition products appear due to the degradation reaction of furfural at long times. These operational conditions are not absolutely important because they are located on times far from the optimum of xylooligosaccharide production. On the other hand, the decomposition products (DP) value is quite low and it is calculated by difference with respect the total composition. Then, the experimental errors that can be commited are significant.

**6. Types of Reactions.** Practically all kinetic models developed for this type of treatment take into account first-order irreversible reactions.

On the basis of these factors, the kinetic model shown in Figure 2 is proposed. This model corresponds basically to those developed for the autohydrolysis of other materials[32,33] but, to our knowledge, it is the first time that the fraction of uronic acids has been included in the model. This is important, given that it is believed that uronic acids may be one of the causative factors, together with acetic acid, of the process of autohydrolysis.[35] The model considers the evolution of the four fractions detected separately in the hemicelluloses of *Arundo donax*, since this approach allows for a simple way of calculating the concentrations and compositions of the different kinds involved (hemicelluloses, oligomers, etc) and the values for the kinetic parameters give us a more exact measure of the behavior of the four fractions. In the case of furfural, it is necessary to take into account its joint generation from arabinose and xylose. The analytical protocols used do not allow differentiation between uronic acids bound to oligomers and free uronic acids; if this should be possible, the kinetic model would be equally valid with minimal adjustments.

All variables are stated in gram equivalents of polymers (xylan, araban, acetyl groups, or uronic acids) per 100 g of raw material on a dry basis (see Definition of Variables section). On the basis of the proposed kinetic model, the obtained equation are shown in the appendix.

Two strategies have been applied for the kinetics of the autohydrolysis of *Arundo donax* through pseudo-homogeneous kinetic models:

(1) The experiments conducted at each temperature (9−11 experiments at temperatures of 150, 165, 180, and 195 °C) have been modeled separately, obtaining values of $\alpha_X$, $\alpha_{Ar}$, $\alpha_{AG}$, $\alpha_U$, and $k_1$−$k_{11}$ for each temperature and subsequently comparing the values of the susceptible fractions and applying Arrhenius' equation to calculate the pre-exponential factors $k_{1\_0}$−$k_{11\_0}$ and the activation energies $E_{a1}$−$E_{a11}$. The calculation scheme for obtaining the optimum values of the susceptible fractions and the kinetic coefficients is similar to the one performed in other works.[22]

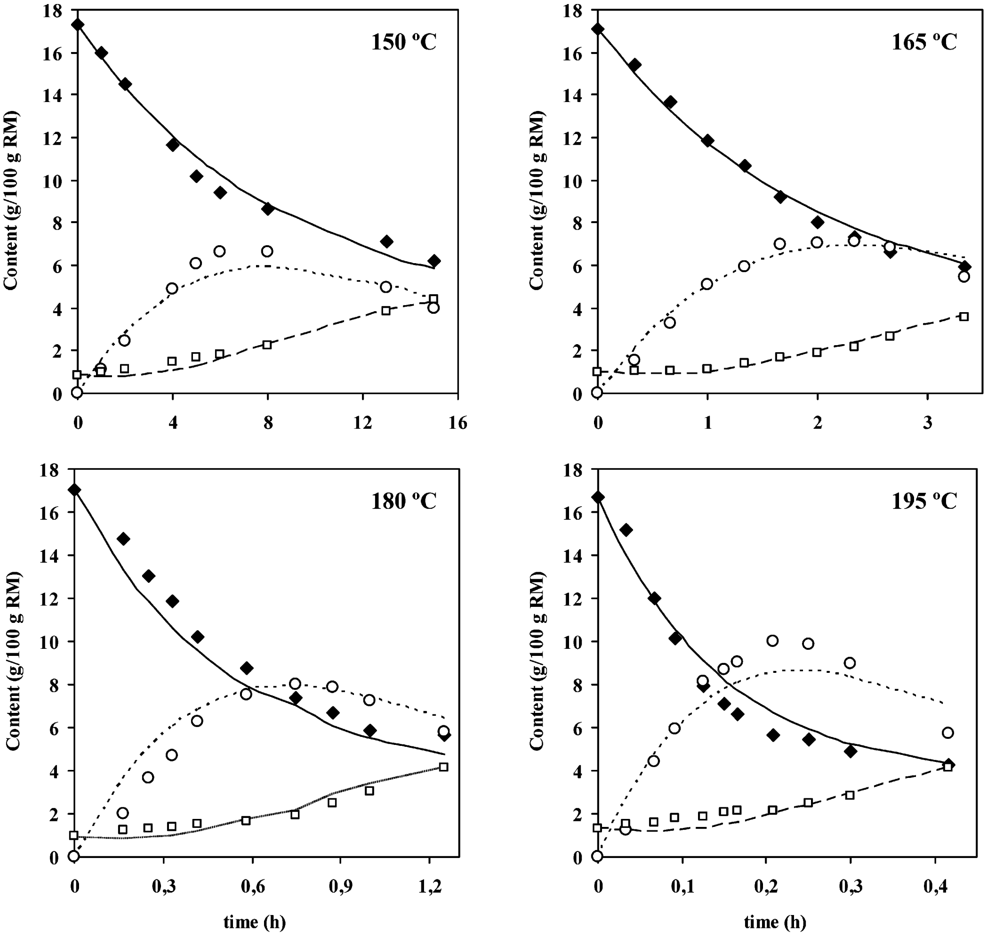

**Figure 6.** Experimental (symbols) and calculated (lines) time courses of xylan remaining in the solid phase (Xn: ◆, —), xylooligosaccharides (XO: ○, - - - -), and xylose (X: □, — — —).

(2) All experiments have been modeled jointly, obtaining unique values of $\alpha_X$, $\alpha_{Ar}$, $\alpha_{AG}$, $\alpha_U$, and the pre-exponential factors $k_{1\_0}-k_{11\_0}$ and activation energies $E_{a1}-E_{a11}$.

Applying the first of these strategies, it was observed that the values of the susceptible fractions did not display any variation either individually or systematically with the temperature (data not shown). This was found previously,[22,32] so that it was decided to use a single susceptible fraction value for strategy 1, demonstrating that there was practically no loss of precision in the adjustment. Table 1 shows the estimated values for the different parameters, as well as the $R^2$ statistical coefficients. In Table 2, the pre-exponential factors, activation energies, and $R^2$ values are shown that result from the adjustment of the data in Table 1 by Arrhenius equations.

To carry out the generalized adjustment for all the experiments, a calculation scheme has been followed that is shown in Figure 3, which summarizes the algorithm employed to estimate the set of kinetic parameters for xylan and araban; the scheme for the acetyl groups and the uronic acids is a simplification of that used for the pentoses. In this protocol, the data from Table 2 have been used as trial values. The results of the generalized adjustment are shown in Table 3. In Figures 4−8, the comparison between the experimental values and the calculated values is shown, in which a considerable degree of agreement can be observed, confirming the validity of the model employed. For comparison of the data from Tables 1 and 2 with those of Table 3, it can be seen that there is practically no difference in the values of the susceptible fractions, pre-exponential factors, and activation energies. It should be emphasized that in a first attempt a value was obtained of $\alpha_{Ar} = 0.963$ (very close to the value of 0.940 which is shown in Table 1) and it was decided to establish this parameter at $\alpha_{Ar} = 1.000$ (all araban is susceptible to hydrolysis) on the grounds that, in addition to having to calculate one less parameter, in various experiments of long duration residual araban in the solid was undetectable. No important differences are observed between using $\alpha_{Ar} = 0.963$ (data not shown) with respect to $\alpha_{Ar} = 1.000$.

The adjustment for xylan is satisfactory both for residual xylan as well as for xylooligosaccharides and for xylose. As far as araban is concerned, we see that the adjustment is less precise, but the tendencies for residual araban, ArO and Ar, are adequately predicted. This lack of precision, which is also reflected in the $R^2$ values, is a result of the low content of the raw material in araban. The adjustment both for acetyl groups as well as uronic acids is also satisfactory for all temperatures and times. Uronic acids and acetyl groups are the precursors of the autohydrolysis process. If there is a different time course of these precursors, the variation with time of the components and their decomposition rates would not be the same but the kinetic model would continue being right; so, a new set of kinetic parameters would be obtained.

Furfural and the decomposition products are adjusted based on the data for xylan and araban, and an excellent prediction for furfural can be observed, though not so good for the decomposition products, especially for long periods. DP is calculated by difference (eq A9) and may be influenced by the experimental errors commited in the measurement of the other variables of eq A9. We believe that this failure of prediction for long periods may be due to the existence of other reactions

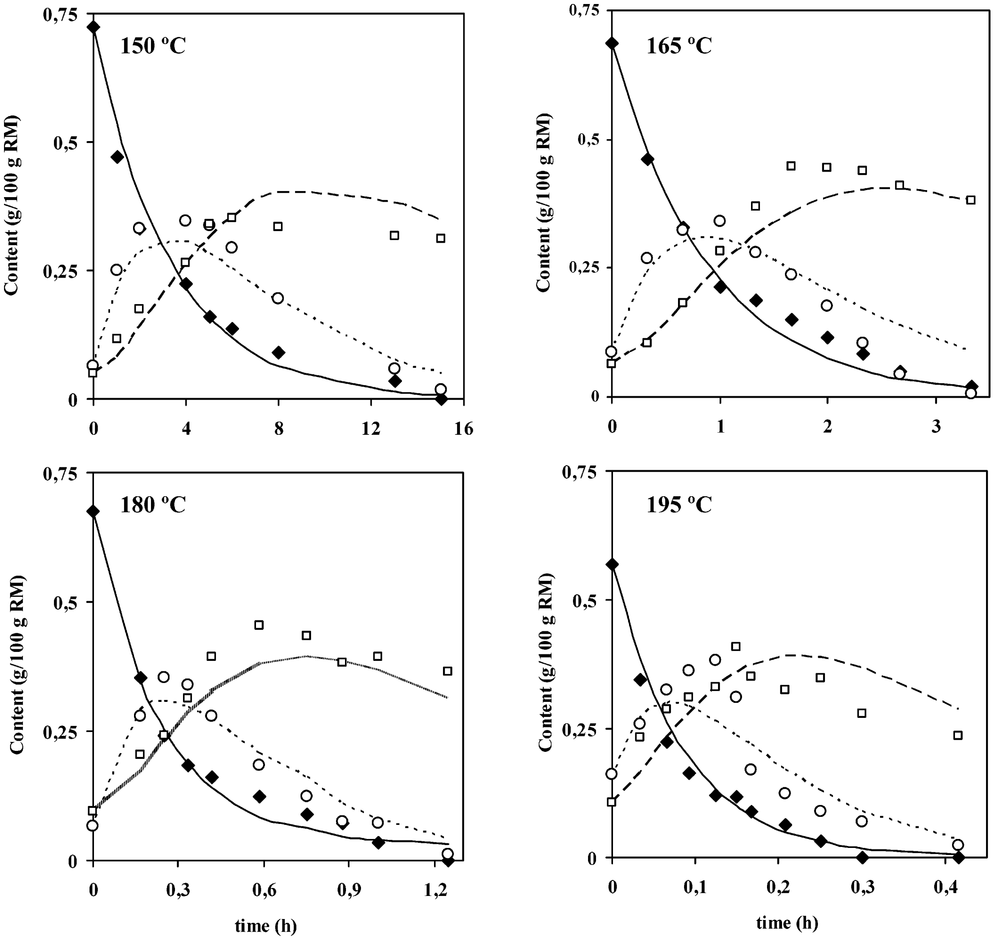

**Figure 7.** Experimental (symbols) and calculated (lines) time courses of araban remaining in the solid phase (Arn: ◆, —), arabinose linked to oligomers (ArO: ○, - - - -), and arabinose (X: □, — — —).

of minor importance to this study, which take place in severe conditions in which the quantity of oligomers is low.

The maximal fraction of xylan converted to XO increases with temperature until it reaches a value equivalent to 55% of the initial xylan at 195 °C. As for the araban, a maximum of 35−40% becomes ArO, without a clear dependence on temperature. The fraction of acetyl groups bound to oligomers shows a maximum value of 38% at 180 °C. On the basis of the data in Table 1, the maximal fraction of xylan converted to XO at different temperatures can be calculated, noting that in order to reach 60%, temperatures of 240 °C or greater are needed, which would increase the cost of the process and would probably give rise to other reactions, in view of which 55% of the initial xylan is a good result.

The value $\alpha_X = 0.802$ is similar to that obtained for eucalyptus, 0.843;[20] brewery's spent grain,[33] with an average value of $\alpha_X = 0.800$; or corncobs,[22] with an average value of $\alpha_X = 0.859-0.897$. In models with two fractions of reactive xylan for corncobs, values of $\alpha_X = 0.803$ were found.[38] The activation energy for xylan, $E_{a1} = 149$ kJ mol$^{-1}$, is close to the values found for the hydrolysis of eucalyptus, 146 kJ mol$^{-1}$, and greater than the values found for corncobs, on the order of 130 kJ mol$^{-1}$,[22] or for brewery spent grain, 108 kJ mol$^{-1}$.[33] In hydrolysis of xylan from hardwoods, the activation energies fall in a range of 103−143 kJ mol$^{-1}$.[39] Comparison of the pre-exponential factors shows values of the same order for eucalyptus, $\ln k_0 = 41.0$ h$^{-1}$,[20] and lower values for corncobs, $\ln k_0 = 36.2$ h$^{-1}$,[22] or brewery spent grain, $\ln k_0 = 30.2$ h$^{-1}$.[33] The comparison of kinetic parameters for other reactions and other hemicellulosic fractions is complex owing to the different kinetic models proposed and the few studies found in the literature.

**3.3. Kinetic Model Using the Severity Factor.** The severity factor or reaction ordinate ($R_o$) was developed by Chornet and co-workers to obtain a simple and approximate interpretation of the solubilization of hemicelluloses.[40] Subsequently, it was adopted for its application in nonisothermal systems and for systems with catalysts present.[41] It is a parameter commonly used to measure the hardness of hydrolytic treatments, especially in cases of autohydrolysis or steam explosion. The main advantage of the use of the severity factor is its simplicity of calculation compared to conventional kinetics. Their inconvenience with their limited capacity for application (only for simple reactions such as that explained below) and the approaches they involve can give rise to greater errors than conventional kinetics.

These severity factors accept that the system behaves with first-order kinetics and that the dependency on temperature follows the Arrhenius equation.

Supposing reagent A participates in an irreversible first-order reaction, the kinetic equation using the severity factor, adapted to take into account the existence of two fractions, one reactive and the other nonreactive, as is the case of this work, is the following

$$\frac{C_A}{C_{A0}} = 1 - \alpha + \alpha \exp(-k_{REF} R_o) \qquad (1)$$

where $C_A$ is the concentration of A, $C_{A0}$ is this concentration at

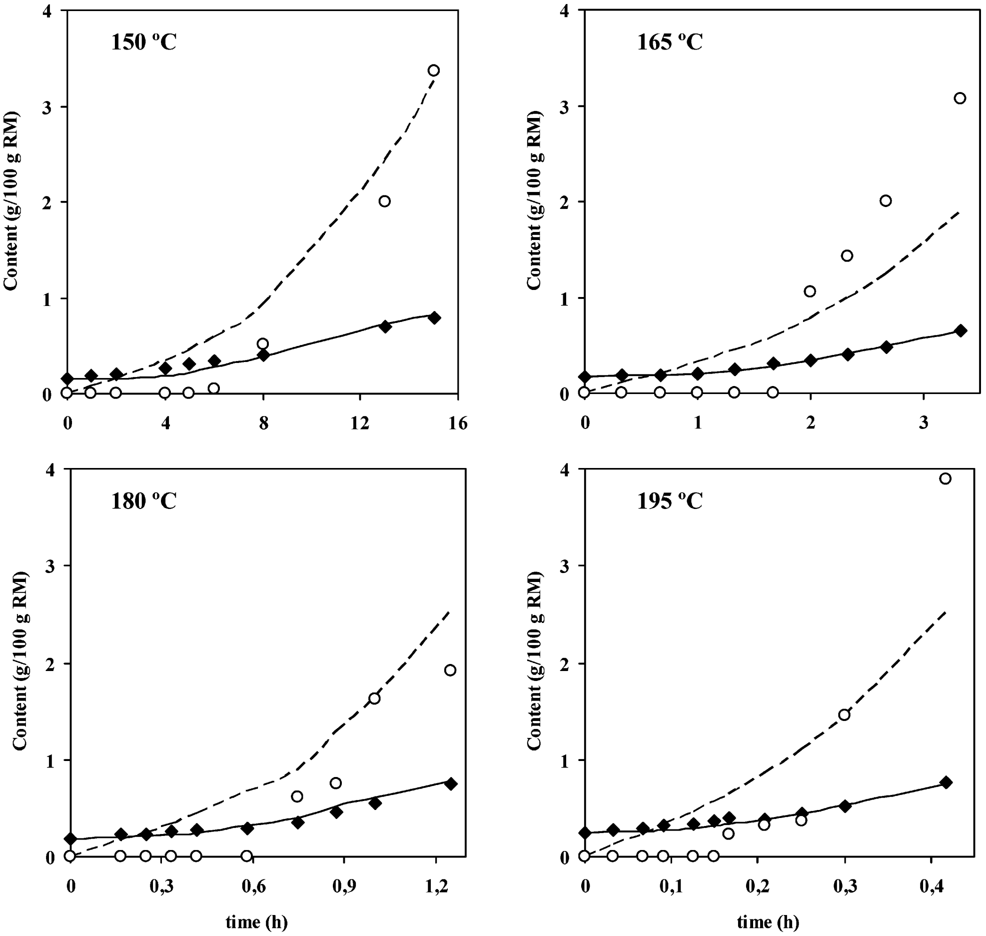

**Figure 8.** Experimental (symbols) and calculated (lines) time courses of furfural (F: ◆, —) and decomposition products (DP: ○, - - - -).

zero-time, α is the fraction susceptible to hydrolysis of A, $k_{REF}$ is the kinetic coefficient evaluated at $T_{REF}$, and $R_o$ is the severity factor, which can be calculated as follows:

$$R_o = \int_0^t \exp\left(\frac{T(t) - T_{REF}}{\omega}\right) dt \qquad (2)$$

and

$$\omega = \left(\frac{RT_{REF}^{\;2}}{E_a}\right) \qquad (3)$$

where $E_a$ is the activation energy.

In conventional kinetics, the conversion produced during the heating was taken into account through values of $t = 0$; with the severity factor, we must take into account the temperature profile that, just as is shown in Figure 1, consists of a first period of heating, an isothermal period, and a period of rapid cooling, so that eq 2 must be modified to include the three periods. Although it is customary only to use the severity factor for the isothermal period, which tends to be the most important time period, this can lead to considerable errors. From the adjustment using $R_o$ which is discussed below, it is found that in experiments where $t = 0$ (only heating and cooling) at 150 °C, the heating accounts for 99% of $R_o$, whereas at other temperatures this value is approximately 87%, the rest being due to cooling. At 150 °C, heating accounts for less than 2% and cooling accounts for less than 0.1%. At 165 and 180 °C, heating only has importance for short periods, where it accounts for up to 12% of the total severity, while cooling is always less than 2%. At the highest experimental temperature, and where the greatest quantity of oligomers is obtained, heating may account for up to 41% and cooling for 6%. It should be emphasized that these values are always for short periods, and if we notice the periods in which the maximum quantity of oligomers is obtained, we see that at 150 and 165 °C heating accounts for less than 1% of the total severity; at 180 °C, this value is 3%, and at 195 °C, heating and cooling account for 11% and 2%, respectively, of the total severity.

**Table 4. Susceptible Fractions ($\alpha_i$), Pre-exponential Factors ($k_{0i}$), Activation Energies ($E_{ai}$), and Statistical Parameter $R^2$ for Hemicellulose Solubilization Using the Severity Factor Approach**

| | $\alpha_i$ (dimless) | ln $k_0i$ ($k_{0i}$ in $h^{-1}$) | $E_a i$ (kJ $mol^{-1}$) | $R^2$ |
|---|---|---|---|---|
| xylan | 0.802 | 38.2 | 142 | 0.969 |
| araban | 1.000 | 35.2 | 127 | 0.961 |
| acetyl groups | 0.901 | 35.8 | 132 | 0.989 |
| uronic acids | 0.857 | 36.1 | 132 | 0.948 |

The kinetics for the solubilization of xylan, araban, acetyl groups, and uronic acids have been modeled through severity factors. For this, the sum of the squares of the deviations between experimental values and calculated values through eq 3 of the xylan, araban, acetyl groups, and uronic acids content has been minimized. For the purpose of minimizing error, the average temperature of experimentation has been taken as $T_{REF}$ following the recommendations of Chornet and co-workers.[42] In Table 4, the results of the optimization are shown (the susceptible fraction α, the kinetic parameters $k_0$, and $E_a$ and the statistical parameter $R^2$). Once again, the value $\alpha_{Ar} = 1$ has been used (using $\alpha_{Ar}$ as an optimization parameter, the value $\alpha_{Ar} = 0.95$ was obtained, with no special difference in the goodness-of-fit). Comparing the data utilizing the severity factor with those obtained utilizing the conventional kinetics (Table

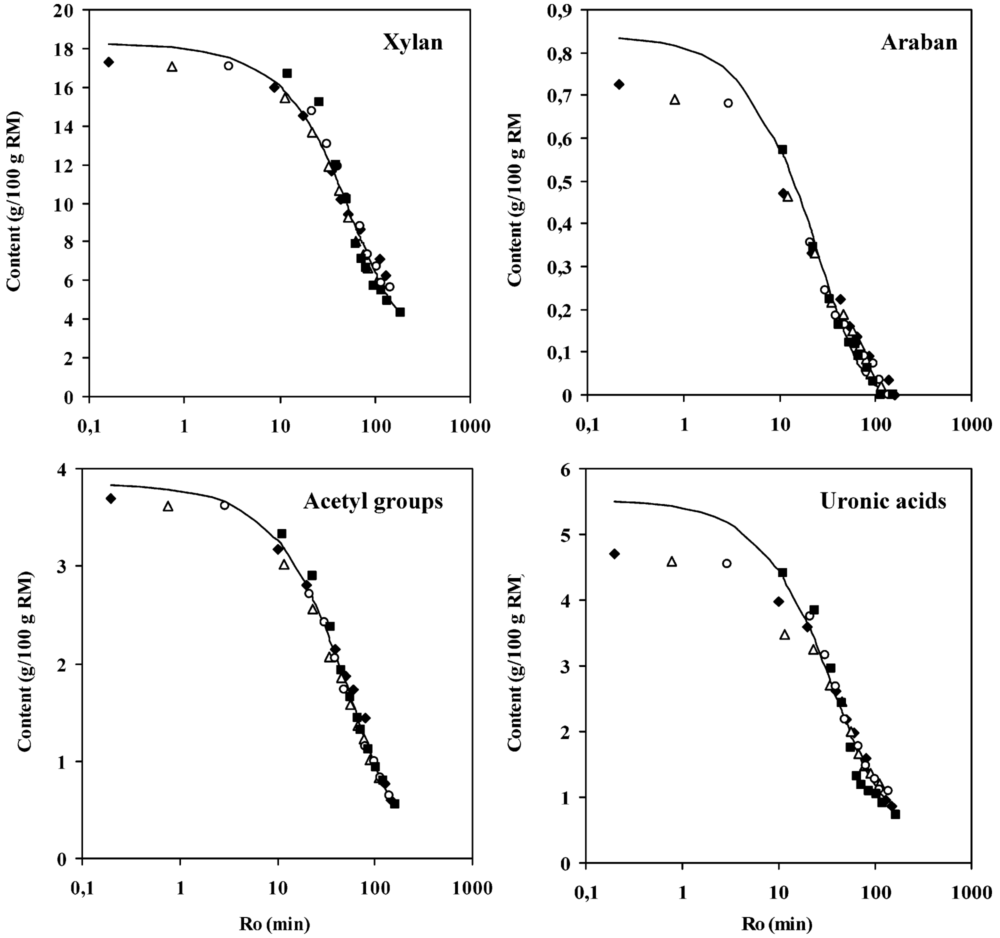

**Figure 9.** Experimental (symbols) and calculated (lines) values of acetyl groups, araban, uronic acids, and xylan remaining in the solid phase (150 °C ◆; 165 °C △; 180 °C ○; 195 °C ■) using the severity factor.

3), it can be observed that very similar values are obtained, with practically identical values for $\alpha_i$ except $\alpha_U$, which is 4% less. The values for the pre-exponential factors and the activation energies are slightly lower than those obtained through conventional kinetics. In Figure 9, the comparison between the experimental and calculated values is shown. It can be seen that there is a high degree of agreement among all the experiments, except for the initial points of araban and uronic acids, where the severity factor produces slightly excessive values. No difference is observed among the experiments performed at different temperatures.

## 4. Conclusions

The isothermal kinetics of the autohydrolysis of *Arundo donax* L. has been studied for the purpose of obtaining mathematical models that allow prediction of concentrations of the different compounds involved in the process. A kinetic model has been developed based on parallel and consecutive, pseudo-homogeneous, first-order, irreversible reactions with Arrhenius equation temperature dependence. This model takes into account the complex nature of hemicelluloses (considering the existence of four fractions in the raw material: xylan, araban, acetyl groups, and uronic acids) which adequately describes the time course of xylan, araban, acetyl groups, xylooligosaccharides, arabinosaccharides, acetyl groups linked to oligomers, acetic acid, arabinose, uronic acids, xylose, furfural, and decomposition products. The kinetic model developed gives a good interpretation of the experimental data. Diverse strategies for calculating the model's parameters were applied and compared with those found in the literature. The kinetic adjustment was also carried out using the severity factor approach, proving the agreement of values obtained with conventional kinetics and with the severity factor.

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## Appendix: Kinetic Model Equations

By integration of the kinetic model derived from the mechanism shown in Figure 2, one arrives at the following:

$$\mathrm{Xn} = C_1 \exp(-k_1 t) + C_2 \tag{A1}$$

$$\mathrm{XO_H} = C_3 \exp(-k_1 t) + C_4 \exp(-k_2 t) \tag{A2}$$

$$\mathrm{XO_L} = C_5 \exp(-k_1 t) + C_6 \exp(-k_2 t) + C_7 \exp(-k_3 t) \tag{A3}$$

$$\mathrm{X} = C_8 \exp(-k_1 t) + C_9 \exp(-k_2 t) + C_{10} \exp(-k_3 t) + C_{11} \exp(-k_4 t) \tag{A4}$$

$$\mathrm{Arn} = C_{12} \exp(-k_6 t) + C_{13} \tag{A5}$$

$$\mathrm{ArO} = C_{14}\exp(-k_6 t) + C_{15}\exp(-k_7 t) \tag{A6}$$

$$\mathrm{Ar} = C_{16}\exp(-k_6 t) + C_{17}\exp(-k_7 t) + C_{18}\exp(-k_8 t) \tag{A7}$$

$$\mathrm{F} = C_{19}\exp(-k_1 t) + C_{20}\exp(-k_2 t) + C_{21}\exp(-k_3 t) + C_{22}\exp(-k_4 t) + C_{23}\exp(-k_6 t) + C_{24}\exp(-k_7 t) + C_{25}\exp(-k_8 t) + C_{26}\exp(-k_5 t) \tag{A8}$$

$$\mathrm{DP} = \mathrm{Xn}_{\mathrm{RM}} + \mathrm{Arn}_{\mathrm{RM}} - \mathrm{Xn} - \mathrm{XO}_{\mathrm{H}} - \mathrm{XO}_{\mathrm{L}} - \mathrm{X} - \mathrm{Arn} - \mathrm{ArO} - \mathrm{Ar} - \mathrm{F} \tag{A9}$$

$$\mathrm{Acn} = C_{27}\exp(-k_9 t) + C_{28} \tag{A10}$$

$$\mathrm{AcO} = C_{29}\exp(-k_9 t) + C_{30}\exp(-k_{10} t) \tag{A11}$$

$$\mathrm{AcH} = \mathrm{Acn}_{\mathrm{RM}} - \mathrm{Acn} - \mathrm{AcO} \tag{A12}$$

$$\mathrm{UAn} = C_{31}\exp(-k_{11} t) + C_{32} \tag{A13}$$

$$\mathrm{UA} = \mathrm{UAn}_{\mathrm{RM}} - \mathrm{UAn} \tag{A14}$$

Where, the constants are calculated as follows:

$$C_1 = \beta_{\mathrm{X}}\mathrm{Xn}_0 \tag{A15}$$

$$C_2 = (1 - \beta_{\mathrm{X}})\mathrm{Xn}_0 \tag{A16}$$

$$C_3 = \frac{k_1 C_1}{k_2 - k_1} \tag{A17}$$

$$C_4 = \mathrm{XO}_{\mathrm{H0}} - C_3 \tag{A18}$$

$$C_5 = \frac{k_2 C_3}{k_3 - k_1} \tag{A19}$$

$$C_6 = \frac{k_2 C_4}{k_3 - k_2} \tag{A20}$$

$$C_7 = \mathrm{XO}_{\mathrm{L0}} - C_5 - C_6 \tag{A21}$$

$$C_8 = \frac{k_3 C_5}{k_4 - k_1} \tag{A22}$$

$$C_9 = \frac{k_3 C_6}{k_4 - k_2} \tag{A23}$$

$$C_{10} = \frac{k_3 C_7}{k_4 - k_3} \tag{A24}$$

$$C_{11} = \mathrm{X}_0 - C_8 - C_9 - C_{10} \tag{A25}$$

$$C_{12} = \beta_{\mathrm{Ar}}\mathrm{Arn}_0 \tag{A26}$$

$$C_{13} = (1 - \beta_{\mathrm{Ar}})\mathrm{Arn}_0 \tag{A27}$$

$$C_{14} = \frac{k_6 C_{12}}{k_7 - k_6} \tag{A28}$$

$$C_{15} = \mathrm{ArO}_0 - C_{14} \tag{A29}$$

$$C_{16} = \frac{k_7 C_{14}}{k_8 - k_6} \tag{A30}$$

$$C_{17} = \frac{k_7 C_{15}}{k_8 - k_7} \tag{A31}$$

$$C_{18} = \mathrm{Ar}_0 - C_{16} - C_{17} \tag{A32}$$

$$C_{19} = \frac{k_4 C_8}{k_5 - k_1} \tag{A33}$$

$$C_{20} = \frac{k_4 C_9}{k_5 - k_2} \tag{A34}$$

$$C_{21} = \frac{k_4 C_{10}}{k_5 - k_3} \tag{A35}$$

$$C_{22} = \frac{k_4 C_{11}}{k_5 - k_4} \tag{A36}$$

$$C_{23} = \frac{k_8 C_{16}}{k_5 - k_6} \tag{A37}$$

$$C_{24} = \frac{k_8 C_{17}}{k_5 - k_7} \tag{A38}$$

$$C_{25} = \frac{k_8 C_{18}}{k_5 - k_8} \tag{A39}$$

$$C_{26} = \mathrm{F}_0 - C_{15} - C_{16} - C_{17} - C_{18} - C_{23} - C_{24} - C_{25} \tag{A40}$$

$$C_{27} = \beta_{\mathrm{AG}}\mathrm{Acn}_0 \tag{A41}$$

$$C_{28} = (1 - \beta_{\mathrm{AG}})\mathrm{Acn}_0 \tag{A42}$$

$$C_{29} = \frac{k_6 C_{27}}{k_7 - k_6} \tag{A43}$$

$$C_{30} = \mathrm{AcO}_0 - C_{29} \tag{A44}$$

$$C_{31} = \beta_{\mathrm{U}}\mathrm{UAn}_0 \tag{A45}$$

$$C_{32} = (1 - \beta_{\mathrm{U}})\mathrm{UAn}_0 \tag{A46}$$

The subscripts used are as follows: RM = raw material; 0 = beginning of the isothermal stage; X = xylan; Ar = araban; AG = acetyl groups; U = uronic acid.

The easy fraction in the raw material (α, 0 ≤ α ≤ 1) represents the masic fraction in the raw material that is susceptible to be solubilized and relates to the soluble fraction in zero time ($\beta$) through the following equations:

$$\text{Xylan:}\quad \beta_{\mathrm{X}} = 1 - (1 - \alpha_{\mathrm{X}})\frac{\mathrm{Xn}_{\mathrm{RM}}}{\mathrm{Xn}_0} \tag{A47}$$

$$\text{Araban:}\quad \beta_{\mathrm{Ar}} = 1 - (1 - \alpha_{\mathrm{Ar}})\frac{\mathrm{Arn}_{\mathrm{RM}}}{\mathrm{Arn}_0} \tag{A48}$$

$$\text{Acetyl groups:}\quad \beta_{\mathrm{AG}} = 1 - (1 - \alpha_{\mathrm{AG}})\frac{\mathrm{Acn}_{\mathrm{RM}}}{\mathrm{Acn}_0} \tag{A49}$$

$$\text{Uronic acid:}\quad \beta_U = 1 - (1 - \alpha_U)\frac{UAn_{RM}}{UAn_0} \tag{A50}$$

Since $XO_H$ and $XO_L$ were measured together, their contribution was measured by

$$XO = XO_H + XO_L \tag{A51}$$

### Definition of Variables

Xn = xylan remaining in the solid phase
Arn = araban remaining in the solid phase
Acn = acetyl groups remaining in the solid phase
UAn = uronic acids remaining in the solid phase
XO = xylooligosaccharides
ArO = arabinose linked to oligomers
AcO = acetyl groups linked to oligomers
X = xylose
Ar = arabinose
AcH = acetic acid
UA = uronic acids in liquid phase
F = furfural
DP = decomposition products

*Subscripts*

H = high molecular weight (refers to XO)
L = low molecular weight (refers to XO)
s = fraction of polymer susceptible to solubilization

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# *Arundo donax* L. Valorization under Hydrothermal and Pulp Processing

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This paper will consider the influence of hydrothermal pretreatment to obtain a valuable liquid phase and suitable raw material for pulping from *Arundo donax* L. and the influence of the operating conditions used in the organosolv pulping of the *Arundo donax* L. autohydrolysis process (viz., ethanol concentration, temperature, and pulping time) on the yield, kappa index, viscosity, and glucan content of the resulting pulp to determine the best pulping conditions. From autohydrolysis, a valuable liquid phase could be obtained. Maximum glucose and xylose contents have been obtained at 180 °C. Suitable characteristics of pulps and acceptable yield, viscosity, and kappa index values could be obtained by operating at high temperature (200 °C), pulping time (130 min), and ethanol concentration (60%). The yields and kappa index values found for pulps from solid residues of *Arundo donax* L. autohydrolysis were similar to those found for other *Arundo donax* L. pulps.

## 1. Introduction

Lignocellulosic materials are the most important renewable resources of the terrestrial ecosystem and have been used for many biological and industrial purposes. In that form, there is a growing interest in new processes to refine lignocellulosic materials under environment-friendly technologies, such as autohydrolysis (based on the utilization of water as the sole fractionation agent).[1−3] The autohydrolysis process provides access to various wood components (glucose, mannose, galactose, arabinose, xylose, etc.) and creates, in the water soluble fraction, a versatile mixture of easily fermentable carbohydrates (hemicellulosic sugars) for a host of commercially valuable organic chemicals.[1,4]

The solid fraction, rich in cellulose and lignin, can be used as a raw material for the pulp industry, for alcohol production or as a ruminant feed. In that form, the most valuable alternative to these products is the use as raw material for pulp and papermaking.

On the other hand, the trend for modern fine papermaking is to develop short fibers rather than to cut long fibers and then develop those.[5] Hardwood can yield a well formed strong sheet, to a point where softwood and hardwood pulps give nearly identical properties.[6] In this way, the use of nonwoody faster-growing species for papermaking could have a great advantage in that they provide remediation for the environmental problems associated with the industrial use of that vegetable species.

With this perspective, *Arundo donax* L. (Gigant reed), a stout perennial grass, with thick, short, branched rhizomes and culms up to 6 m tall has a rapid growth rate and strong vegetative competitive ability which enable it to that industrial use. Its cane has been suggested for biomass for energy,[7] and its stems are harvested for use in papermaking and other industrial uses.[8]

*Arundo donax* L. grows best along river banks and in other wet places and is best developed in poor sandy soil and in sunny situations. It is said to tolerate all types of soils, from heavy clays to lose sands and gravelly soils. *Arundo donax* L. is reported to tolerate annual precipitation of 3−40 dm, an annual temperature of 9−28.5 °C, and a pH of 5.0−8.7.[9,10] According to Duke,[11] its annual productivity ranges from 10−59 Mt/ha. In addendum, Westlake[12] cites evidence that *Arundo donax* L. can produce 40−75 Mt/(ha year) in warm temperate and tropical regions.

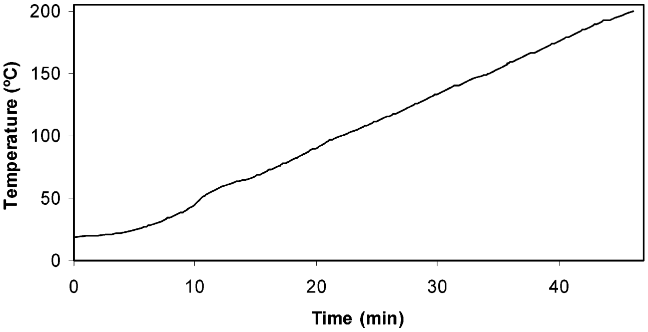

**Figure 1.** Temperature profile in the reactor during the heating process.

The most desirable approach is that of an integrated, value-added management plan. This involves the optimum use of all wood compounds to maxima valorization. In cases where more than one valorization technique is used, the various techniques should be compatible with one another. With this perspective, a hydrothermal pretreatment and subsequent pulping process could be an effective, economical, environmentally friendly value-added strategy.

This paper deals with the influence of hydrothermal pretreatment to obtain a valuable liquid phase and suitable raw material for subsequent pulping and the influence of the operating conditions used in the organosolv pulping of the *Arundo donax* L. autohydrolysis process (viz., ethanol concentration, temperature, and pulping time) on the yield, kappa index, viscosity, and glucan content of the resulting pulp to determine the best pulping conditions.

## 2. Experimental Section

**2.1. Hydrothermal Pretreatment Procedure.** Wood chips and water were mixed in the desired proportions and reacted in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated (from 150 to 200 °C, Table 3) with external mantles. In Figure 1, the temperature

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profile during the heating process of the reactor has been shown. The reaction media were heated during the desired time, depending on the required temperature (Figure 1), and then cooled. After achieving normal pressure (monitored by a barometer implemented in the reactor), the reactor was opened and samples of the suspensions were withdrawn. The solid/liquid ratio was fixed (1/8) and held constant in all experiments. This value is, among practiced values, the minimum value that allows a homogeneous mixture. At the end of treatment, the solid residues were recovered by filtration and washed with distilled water. A fraction was used for pulping, and another fraction was air-dried and milled to a particle size < 0.5 mm. Milled samples were assayed for cellulose, hemicellulose, lignin, and acetyl groups using the same methods as for raw material analysis. An aliquot of liquors was filtered through 0.45 $\mu$m membranes and used for direct high-performance liquid chromatography (HPLC) determination of monosaccharides, furfural, and acetic acid. A second aliquot of liquors (25 mL) was subjected to quantitative posthydrolysis (with 4% $H_2SO_4$ at 121 °C during 60 min) before HPLC analysis. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers[13] and acetyl groups bound to oligosaccharides.

**2.2. Pulping Procedure.** The method called the organosolv process has been used by adding ethanol to a water basis. Under this process, pulps with high yield, low residual lignin content, high brightness, and good strength properties can be produced. The pulps can be bleached without chlorine chemicals, and their strength properties are similar to those of kraft and sulfite pulps.[14]

Cellulose pulps were obtained in the same reactor used in hydrothermal pretreatment. The initial liquor/solid ratio was 8/1 (dry weight basis), the ethanol concentration in the cooking liquor ranged from 20, 40, and 60 wt %, the temperature ranged from 160, 170, 180, 190, and 200 °C, and the pulping time ranged from 30, 55, 80, 105, and 130 min. The reactor was then closed and simultaneously heated and actuated to ensure good mixing and uniform swelling of *Arundo donax* L.

When the pulping time was finished, the reactor was chilled, establishing the temperature of the controller to 25 °C.

Following cooking, the pulp was separated from the liquor and disintegrated, without disturbing the fibers, during 3 min, washed on a sieve of 0.16 mm mesh, defibered, and passed through a strainer filter (0.4 mm mesh) in order to isolate the uncooked material.

**2.3. Characterization of the Raw Material, Pulp.** *Arundo donax* L. wood trimmings samples were milled to pass an 8 mm screen, since no diffusional limitations were observed for this particle size in preliminary studies. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored. Aliquots from the homogenized wood lot were subjected to moisture determination (drying at 105 °C to constant weight), quantitative acid hydrolysis with 5 mL of 72% sulfuric acid for an hour, and quantitative posthydrolysis with 4% $H_2SO_4$ (adding water until 148.67 g) at 121 °C during 60 min. Before HPLC analysis, the solid residue from the posthydrolysis stage was recovered by filtration and considered as Klason lignin, sugar degradation, and acid soluble lignin. The monosaccharides and acetic acid contained in the hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar decomposition) the contents of the samples in cellulose (such as glucan), hemicellulose (xylan and araban), uronic acids, and acetyl groups. The moisture of wood was considered as water in the material balances. In that form, α-cellulose is glucan and holocellulose is adding glucan, xylan, araban, and uronic acids. Chromatographic separation was performed using an ion-exchange resin Metacarb 87H column (300 mm × 7.8 mm, Varian, USA) under the following conditions: mobile phase 0.05 mol $l^{-1}$ sulfuric acid, flow rate 0.5 mL/min, column temperature 30 °C. The volume injected was 20 $\mu$L.

Characterization of raw material includes the content of uronic acids,[15] ethanol extractives (Tappi 204), and ashes (Tappi 211).

Characterization experiments of pulps involved the following parameters: pulp yield (Tappi 257), kappa index (Tappi 236), viscosity (Tappi 230). In addition, the chemical composition of pulps was determined using the same methodology that used for raw material.

**2.4. Determination of Sugar, Organic Acids, and Furanic Compounds.** The concentration of glucose, xylose, acetic acid, furfural (as a degradation of xylose), and 5-hydroxymethylfurfural (HMF) (as a degradation of glucose) in the samples was analyzed by high-performance liquid chromatography (HPLC). An Agilent 1100 series (Palo Alto, CA) chromatograph equipped with two detectors, a diode array detector and a refractive index detector, was used for the simultaneous detection of the sugars, organic acids, and furanic compounds. Chromatographic separation was performed using similar conditions as those used in section 2.3.

Detection was performed by scanning from 200 to 700 nm for the detection of organic acids and furanic compounds. Wavelengths used for quantification were 280 nm for furfural and 5-hydroxymethylfurfural and 210 nm for organic acids. Identification of individual compounds was carried out by comparing their retention times and spectra with those of original standards. Quantitative determinations were carried out with a standard external calibration method.

**2.5. Statistical Analysis by the Adaptative Network-Based Fuzzy Inference System (ANFIS).** Fuzzy modeling, based on the pioneering idea of Zadeh,[16] is a powerful tool to describe the behavior of nonlinear complex systems. Since the 1980s, fuzzy theory has been successfully applied to the simulation and control of fermentation processes.[17−19] A few other workers have applied fuzzy theory to an anaerobic digestion system.[20]

Another powerful tool for modeling these complex systems is a neural network (NN), which was developed from the analogies to the properties of biological neurons. The most important feature of neural networks is their ability to achieve an accurate nonlinear mapping from input−output pairs of data without knowing their functional relationship.[21] NNs have been successfully applied to many areas of assessing biological systems, such as anaerobic digestions,[21−24] fermentation processes,[25,26] etc.

The integration of fuzzy systems and neural networks can combine the merits of both systems and offer a more powerful tool for modeling. A neural fuzzy system is such an integrated system modeling. It uses NNs as tools in fuzzy systems.

In that form, the adaptive network-based fuzzy inference system (ANFIS), proposed by Jang,[27] is based on the first-order Sugeno fuzzy model. The NN paradigm used is a multilayer feed-forward back-propagation network. An adaptive network that is functionally equivalent to a Sugeno fuzzy model has been constructed. The adaptive network can tune the fuzzy system with a back-propagation algorithm based on the collection of input−output data. This provides the fuzzy system with the ability to learn. The detailed architecture and learning procedure for ANFIS can be found in the related literature.[28,29]

**Table 1. Content of α-Cellulose, Holocellulose, and Lignin in *Arundo donax* (Arundo) and *Eucalyptus globulus* (EG)**

| percentages oven dry matter basis[a] | Arundo | | | | EG |
|---|---|---|---|---|---|
| | present study | Shatalov and Pereira[30] | Ververis et al.[31] | Shatalov and Pereira[32] | Garrote et al.[33] |
| α-cellulose (%) | 34.8 (5.6) | 30.50 | 30.8 | 32.93 | 46.8 |
| holocellulose (%) | 64.5 (7.3) | 39.54 | 62.7 | 61.41 | 66.9 |
| lignin (%) | 23.0 (4.6) | 15.8−22.0 | 17.1 | 19.56 | 22.9 |

[a] Standard deviations are shown within parentheses.

**Table 2. Chemical Composition of Arundo and Other Pulp Raw Materials**

| percentages oven dry matter basis[a] | present study | wheat straw[34] | miscanthus[35] | cotton gin waste fibers[36] | EG[33] | EG[37] |
|---|---|---|---|---|---|---|
| ash (%) | 3.0 (0.3) | 9.6 | 2.0 | 10.46 | 1.2 | |
| EtOH extr. (%) | 9.1 (1.4) | 5.3 | 4.2 | 7.7 | 0.6 | 1.72 |
| glucan (%) | 34.8 (5.6) | 55.4 | 39.5 | 37.1 | 46.8 | 53.4 |
| xylan (%) | 19.4 (2.3) | 34.6 | 19 | 9.41 | 16.6 | 14.2 |
| araban (%) | 1.5 (0.0) | 5.6 | 1.8 | 2.3 | 0.54 | 0.4 |
| acetil groups (%) | 3.4 (0.2) | | | | 3.56 | |
| uronic acids (%) | 5.5 (0.3) | | 1.8 | | | |

[a] Standard deviations are shown within parentheses.

The mathematical equation which responds to different rules is the following:

$$y_e = \frac{\sum_{l=1}^{m} y_l R_l}{\sum_{l=1}^{m} R_l} \qquad (1)$$

where $y_e$ = estimate value of output variable, $m$ = number of rules, $y_l$ = defuzzifier, and $R_l$ = product of the selected membership functions.

## 3. Results and Discussion

**3.1. Raw Material Characteristics.** All *Arundo donax* L. (Arundo) raw material samples were taken from La Rábida (Huelva, Spain). In Table 1, a comparison of α-cellulose, holocellulose, and lignin contents in other Arundo raw materials and with those in *Eucalyptus globulus* (EG), used as reference, has been made. These values were similar to those obtained for other authors. However, that table shows certain variations in properties, and this indicates that uncontrollable factors such as weather and water availability play a significant role in controlling the measured properties. With respect to EG, lower contents in α-cellulose and holocellulose and similar contents in lignin have been found.

In Table 2, comparisons with other alternative cellulose pulp raw materials (wheat straw, miscanthus, and cotton gin waste) and with EG have been made.

As can be seen, Arundo yielded lower ash percentages, similar to miscanthus and EG. On the contrary, the EtOH extractables content is higher than those found for other materials. The glucan content of Arundo was comparable to those obtained for miscanthus and cotton gin waste. However, the Arundo glucan content shows lower values with respect to wheat straw and EG. The arabinan and acetil groups contents found are similar to each other except those of wheat straw. In this raw material, the highest arabinan content has been found with respect to the others materials shown. Xylan and arabinan contents show slightly higher values than those found for EG.

The chemical characteristics of Arundo and eucalyptus wood are similar in ash, holocellulose, lignin, xylan, and acetyl groups. However, the content in EtOH extractables is higher for Arundo than those found for others raw materials.

**Table 3. Composition of the Liquid Phase from the Nonisothermal Autohydrolysis Treatment of *Arundo donax*[a]**

| T (°C) | 150 | 160 | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|---|---|
| xylooligomers (%) | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.63 | 2.38 | 2.55 | 5.73 |
| glucose (%) | 0.02 | 0.01 | 0.02 | 1.02 | 1.10 | 1.13 | 0.88 | 0.77 | 0.86 |
| xylose (%) | 0.01 | 0.01 | 0.18 | 0.66 | 0.78 | 0.92 | 0.72 | 0.63 | 0.70 |
| arabinose (%) | 0.00 | 0.02 | 0.05 | 0.05 | 0.06 | 0.10 | 0.14 | 0.18 | 0.21 |
| formic acid (%) | 0.00 | 0.00 | 0.00 | 0.03 | 0.04 | 0.06 | 0.07 | 0.13 | 0.11 |
| acetic acid (%) | 0.54 | 0.46 | 0.30 | 0.68 | 0.71 | 0.83 | 1.25 | 1.74 | 2.31 |
| HMF (%) | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.05 | 0.09 | 0.10 | 0.20 |
| furfural (%) | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.06 | 0.23 | 0.26 | 0.46 |

[a] Percentages are given with respect initial raw material.

This fact could indicate high contents of components that could cause problems related to pitch. Pitch deposits in the manufacturing of pulp represent a complex phenomenon, the incidence of which has increased during recent years.[38,39] Pitch can cause problems by adhering to machinery and reducing the quality of the pulp.

Then, Arundo could be an adequate raw material for hydrothermal treatment, to obtain extractable and valuable products and minimize pitch deposits, and subsequent pulp processing. Nevertheless, Arundo could obtain a lower pulping yield due to higher amounts of EtOH solubles with respect to EG wood.

**3.2. Hydrothermal Material Characteristics.** In hydrothermal treatment, a nonisothermal autohydrolysis of Arundo was studied to obtain maximum losses of xylan[40] with minimum losses in yield. That operation was carried out at nine different temperatures (150−200 °C).

In Figure 1, yield percentages and solubilized fractions, with respect to raw material, at different temperatures are shown. In this figure, a progressive decrease in yield and, simultaneously, an increase in the solubilized fraction is observed. A higher yield loss has been found from 185 to 200 °C. This could be due to more effective hemicellulose degradation.[41]

A mass balance in the liquid phase obtained from hydrotermal treatments is shown in Table 3. Comparing the liquid phase obtained under those selected conditions (150−200 °C), a greater increment in the content of xylooligomers has been found from 185 to 200 °C. Nevertheless, maximum glucose and xylose contents have been obtained at 180 °C, and after this temperature, a descent in those obtained contents has been observed. Araban, formic acid, acetic acid, HMF, and furfural contents show progressive increase in their respective amounts.

To ensure minimum degradation of the solid phase, with maximum losses of xylan, 185 °C has been selected for an

**Table 4. Composition of the Solid Phase from the 185 °C Nonisothermal Autohydrolysis Treatment of *Arundo donax*[a]**

| | solid phase |
|---|---|
| glucan (%) | 38.09 |
| xylan (%) | 20.62 |
| araban (%) | 0.91 |
| acetyl groups (%) | 3.65 |
| lignin (%) | 26.58 |

[a] Percentages are given with respect initial material raw.

appropriate hydrothermal and later pulping process of the solid phase. Nevertheless, the selected conditions could guarantee a lesser degradation of the fibers with respect to higher temperature (190−200 °C) utilization. Heitz[42] and Garrote,[43,44] at those temperatures, report important cellulosic fiber degradation, due to hydrolysis and autohydrolysis phenomena.

In Table 4, the chemical characterization of the solid phase obtained at 185 °C is shown. Comparing the solid phase obtained under these process conditions and the original raw material (Tables 1 and 2), the percentages of the lignin, cellulose, and hemicellulosic fractions (percentages of xylan and acetyl groups) are similar. The slight increments found in those contents could be produced by a concentration effect.

**3.3. Properties of the Pulp Obtained. Optimization Studies.** The cellulosic material obtained after autohydrolysis was pulped. Many variables can affect organosolv pulping. Many authors have so far used a factorial design to develop empirical models, that maximize process knowledge with a minimum amount of resources, involving several independent variables to identify patterns of variation in the dependent variables (viz., kappa index and viscosity) or various pulping processes as applied to diverse plant materials.[45,46] None, however, has considered the effect of the operating variables on the properties of the pulp obtained from Arundo. These empirical models are to be preferred to theoretical ones as the latter are rather complex when more than two independent variables are involved. In this work, we made best guesses based on the literature and experience.

The standardized values of the independent variables and the properties of obtained cellulose pulps and the paper according to the proposed experimental design are those that appear in Table 5. Each of the shown experimental results (chemical characteristics of pastes) is an average value of at least five determinations. The deviations of each one of those parameters with respect to their averages are smaller than 5% in all of the cases.

By applying an ANFIS analysis for each one of the dependent variables of Table 5 as a function of the independent variables, the mathematical models are obtained (Table 6). These equations can be used to estimate the variation of dependent variables with changes in the independent variables over the ranges considered, on the constancy of the other two variables.

For this study, the optimum numbers of rules have been selected as eight (Table 7), which developing eq 2 yields

$$y_e = \frac{y_1R_1 + y_2R_2 + y_3R_3 + y_4R_4 + y_5R_5 + y_6R_6 + y_7R_7 + y_8R_8}{R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7 + R_8} \qquad (2)$$

Also, a defuzzifier based on the first-order Sugeno fuzzy model

**Table 5. Values of Independent Variables and Properties of the Pulp Obtained in the Organosolv Pulping Process Using the Proposed Experimental Design**

| normalized values[a] | | | | | viscosity | | | acetyl | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ethanol conc | temp | time | yield (%) | kappa index | ($cm^3/g$) | glucan (%) | xylan (%) | groups | holocellulose (%) | lignin (%) |
| 1 | 1 | 1 | 41.36 | 38.75 | 729.3 | 71.05 | 12.89 | 0.69 | 84.63 | 8.68 |
| −1 | 1 | 1 | 23.52 | 141.89 | 122.3 | 74.94 | 3.92 | 0.18 | 79.04 | 18.92 |
| −1 | −1 | 1 | 56.76 | 134.84 | 252.0 | 53.27 | 12.65 | 1.65 | 67.57 | 21.32 |
| 1 | −1 | 1 | 68.48 | 122.07 | 180.8 | 46.17 | 9.13 | 1.72 | 57.02 | 25.84 |
| 0 | 0 | 1 | 49.52 | 91.89 | 410.0 | 67.03 | 8.13 | 0.70 | 75.83 | 15.12 |
| 1 | 1 | −1 | 48.88 | 90.55 | 461.1 | 62.01 | 15.13 | 1.58 | 78.72 | 12.78 |
| −1 | 1 | −1 | 44.35 | 121.80 | 240.0 | 74.21 | 4.90 | 0.27 | 79.38 | 18.84 |
| −1 | −1 | −1 | 56.72 | 130.34 | 186.5 | 48.56 | 14.54 | 2.57 | 65.67 | 24.41 |
| 1 | −1 | −1 | 79.67 | 99.50 | 140.4 | 48.63 | 20.17 | 3.21 | 72.02 | 18.74 |
| 0 | 0 | −1 | 57.42 | 114.89 | 194.1 | 55.02 | 18.11 | 2.44 | 75.57 | 20.18 |
| 0 | 0 | 0 | 45.66 | 72.15 | 392.2 | 64.97 | 10.68 | 1.41 | 77.06 | 16.08 |
| 1 | 0 | 0 | 54.91 | 73.61 | 361.8 | 57.21 | 18.81 | 2.11 | 78.13 | 15.88 |
| 0 | 1 | 0 | 35.23 | 49.09 | 442.5 | 75.24 | 7.38 | 0.34 | 82.96 | 12.12 |
| −1 | 0 | 0 | 49.53 | 114.59 | 353.5 | 64.55 | 6.86 | 0.65 | 72.06 | 21.68 |
| 0 | −1 | 0 | 67.78 | 106.30 | 252.2 | 50.81 | 18.98 | 2.41 | 72.19 | 18.66 |
| 0 | 0 | 0.5 | 50.59 | 74.36 | 383.8 | 66.87 | 12.17 | 1.30 | 80.34 | 16.38 |
| 1 | 0 | 0.5 | 52.89 | 72.99 | 420.6 | 54.67 | 8.44 | 1.75 | 64.86 | 17.10 |
| 0 | 1 | 0.5 | 30.24 | 71.76 | 534.1 | 76.84 | 5.31 | 0.17 | 82.32 | 11.70 |
| −1 | 0 | 0.5 | 47.59 | 121.10 | 387.3 | 70.77 | 7.28 | 0.19 | 78.24 | 19.08 |
| 0 | −1 | 0.5 | 65.56 | 101.91 | 307.5 | 54.97 | 20.8 | 2.61 | 78.38 | 20.02 |
| 0 | 0 | −0.5 | 51.61 | 99.68 | 338.9 | 56.04 | 6.02 | 1.64 | 63.68 | 19.88 |
| 1 | 0 | −0.5 | 63.77 | 98.12 | 315.9 | 54.20 | 15.47 | 2.44 | 72.11 | 17.56 |
| 0 | 1 | −0.5 | 38.13 | 78.16 | 542.7 | 67.06 | 2.91 | 0.91 | 70.87 | 16.68 |
| −1 | 0 | −0.5 | 46.97 | 122.19 | 330.1 | 64.75 | 7.76 | 0.78 | 73.29 | 24.64 |
| 0 | −1 | −0.5 | 68.70 | 110.55 | 198.1 | 50.15 | 22.92 | 2.94 | 76.01 | 20.54 |
| 0 | 0.5 | 0 | 42.34 | 61.17 | 575.2 | 71.20 | 10.33 | 0.72 | 82.25 | 13.14 |
| 1 | 0.5 | 0 | 53.45 | 66.36 | 585.2 | 58.31 | 4.13 | 1.13 | 63.56 | 14.24 |
| 0 | 0.5 | 1 | 42.29 | 68.07 | 510.0 | 74.85 | 8.32 | 0.81 | 83.98 | 15.12 |
| −1 | 0.5 | 0 | 38.39 | 114.27 | 301.8 | 72.35 | 5.03 | 0.15 | 77.53 | 21.88 |
| 0 | 0.5 | −1 | 50.15 | 98.11 | 368.7 | 63.94 | 12.65 | 2.11 | 78.70 | 17.41 |
| 0 | −0.5 | 0 | 57.51 | 101.86 | 357.4 | 54.73 | 17.91 | 2.39 | 75.02 | 18.04 |
| 1 | −0.5 | 0 | 59.79 | 108.26 | 318.5 | 52.67 | 20.67 | 2.64 | 75.98 | 17.72 |
| 0 | −0.5 | 1 | 50.29 | 90.25 | 365.4 | 61.06 | 14.73 | 1.46 | 77.25 | 17.82 |
| −1 | −0.5 | 0 | 55.05 | 123.32 | 341.2 | 58.93 | 10.68 | 1.29 | 70.9 | 23.78 |
| 0 | −0.5 | −1 | 72.61 | 114.41 | 209.3 | 51.11 | 19.64 | 2.80 | 73.54 | 23.38 |

[a] Where non-normalized values of ethanol concentration are 20 (−1), 40 (0), and 60% (1), those of temperature are 160 (−1), 170 (−0.5),180 (0), 190 (0.5), 200 °C (1), and those of time are 30 (−1), 55 (−0.5), 80 (0), 105 (0.5), 130 min (1).

**Table 6. Parameters, for Each One of the Dependent Variables, of the Polynomial Mathematical Models Obtained by ANFIS Analysis on the Proposed Experimental Design**

| rule | $a_l$ | $b_l$ | $c_l$ | $d_l$ |
|---|---|---|---|---|
| | | Yield (%) ($r^2 = 0.982$) | | |
| 1 | 0.10570 | 0.32390 | 0.16170 | 0.00199 |
| 2 | 0.04331 | 0.26880 | 0.10500 | 0.00159 |
| 3 | 0.00069 | 0.21090 | −0.00264 | 0.00111 |
| 4 | −0.02137 | 0.06011 | 0.08412 | 0.00037 |
| 5 | 0.10550 | 0.45100 | 0.06373 | 0.00286 |
| 6 | 0.07767 | 0.20750 | 0.21510 | 0.00149 |
| 7 | 0.08427 | 0.21550 | −0.02379 | 0.00105 |
| 8 | 0.05308 | 0.11120 | 0.10780 | 0.00041 |
| | | Kappa Index ($r^2$=0.975) | | |
| 1 | −0.05102 | 0.82030 | 0.13430 | 0.00315 |
| 2 | −0.77000 | 0.42270 | 0.60140 | 0.00493 |
| 3 | −0.24790 | 0.69360 | −0.34510 | 0.00505 |
| 4 | −0.98310 | 0.43550 | 0.54160 | 0.00035 |
| 5 | 0.18690 | 0.53500 | 0.30620 | 0.00121 |
| 6 | 1.09400 | 0.15520 | 0.21410 | 0.00372 |
| 7 | 0.56720 | 0.38370 | −0.60270 | 0.00362 |
| 8 | 0.78860 | −0.23870 | 0.27020 | −0.00340 |
| | | Viscosity ($cm^3$/g) ($r^2 = 0.934$) | | |
| 1 | 0.16810 | 1.2040 | 1.1320 | 0.00608 |
| 2 | 0.44990 | 1.9140 | 0.2566 | 0.00928 |
| 3 | 0.46960 | 1.3560 | 1.3900 | 0.00794 |
| 4 | 0.59230 | 1.1650 | −0.1149 | 0.00798 |
| 5 | 0.17560 | 0.6218 | 0.6017 | 0.00370 |
| 6 | 0.08533 | 1.1350 | 0.2685 | 0.00584 |
| 7 | 0.36500 | 2.2260 | 1.0480 | 0.01128 |
| 8 | 0.50580 | 2.9320 | 1.3260 | 0.01566 |
| | | Glucan (%) ($r^2 = 0.975$) | | |
| 1 | 0.05327 | 0.27760 | 0.12680 | 0.00159 |
| 2 | 0.06249 | 0.26570 | 0.10520 | 0.00142 |
| 3 | 0.05812 | 0.34830 | 0.14440 | 0.00186 |
| 4 | 0.07772 | 0.30490 | 0.13470 | 0.00172 |
| 5 | 0.06294 | 0.23830 | 0.10220 | 0.00141 |
| 6 | 0.03705 | 0.20970 | 0.09427 | 0.00119 |
| 7 | 0.06452 | 0.27180 | 0.08995 | 0.00143 |
| 8 | 0.04165 | 0.26350 | 0.13700 | 0.00142 |

**Table 7. Selected Rules and Their Respective Liguistic Values**

| rule | ethanol conc | temp | time |
|---|---|---|---|
| 1 | low | low | Low |
| 2 | low | low | high |
| 3 | low | high | low |
| 4 | low | high | high |
| 5 | high | low | low |
| 6 | high | low | high |
| 7 | high | high | low |
| 8 | high | high | high |

has been selected, whose mathematical equation is

$$y_l = a_l c + b_l T + c_l t + d_l \tag{3}$$

where $a_l$, $b_l$, $c_l$, and $d_l$ are the estimated parameters to minimize the error, $c$ is the ethanol concentration, $T$ is the temperature, and $t$ is the pulping time. Additionally, linear membership functions have been selected, with two functions per independent variable, one representing low values and the other one representing high values. The two membership functions for each independent parameter are

$$P_1 = 1 - \frac{1}{p_{\max} - p_{\min}}(p - p_{\min}) \quad \text{(low)} \tag{4}$$

$$P_2 = \frac{1}{p_{\max} - p_{\min}}(p - p_{\min}) \quad \text{(high)} \tag{5}$$

where $P_i$ is the membership function which could be $C_i$ for ethanol concentration ($p_{\max}$ = 60% and $p_{\min}$ = 20%), $T_i$ for temperature ($p_{\max}$ = 200 °C and $p_{\min}$ = 160 °C), and $t_i$ for pulping time ($p_{\max}$ = 130 min and $p_{\min}$ = 30 min).

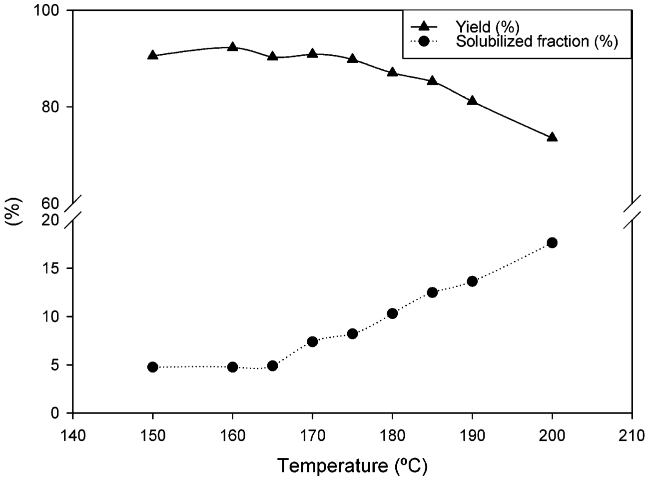

**Figure 2.** Evolution of yield and solubilized fraction percentages as a function of temperature.

$R_l$ is defined by the product of three membership functions (one per independent variable), and the selected combinations of membership functions are

$$R_1 = C_1 T_1 t_1 \tag{6}$$

$$R_2 = C_1 T_1 t_2 \tag{7}$$

$$R_3 = C_1 T_2 t_1 \tag{8}$$

$$R_4 = C_1 T_2 t_2 \tag{9}$$

$$R_5 = C_2 T_1 t_1 \tag{10}$$

$$R_6 = C_2 T_1 t_2 \tag{11}$$

$$R_7 = C_2 T_2 t_1 \tag{12}$$

$$R_8 = C_2 T_2 t_2 \tag{13}$$

Consequently, $y_l$ represents the linear behavior of the system under the conditions of ethanol concentration, temperature, and pulping time defined by $R_l$.

To determine the values of the independent variables giving the optimum yield, kappa index, viscosity, and glucan content, the response surfaces for each dependent variable were plotted at maxima and minima levels of the independent variable most strongly influencing the dependent variables (Figures 2−5).

As can be seen in Figure 2, the pulping temperature is the variable most strongly influencing the yield pulps, and a similar influence has been found for López,[47] Díaz,[48] and Jiménez.[49]

The relatively high effect of the temperature on yield has been considered to be the consequence of the hydrolysis of residual lignin−hemicellulose bonds.[50,51] Also, the yield was less influenced by the ethanol concentration than by the time, and a high positive influence has been found in ethanol concentration. The highest yield (YI = 79.6% with respect to material to pulping process; YI = 69% with respect to initial raw material) is obtained at low values of the pulping temperature, low values of time, and high ethanol concentration. The range yield obtained was higher (with respect to that found by Shatalov and Pereira[52]) than that found in ethanol soda (46.8%), ASAM (46.5%), organocell (45.7%), and kraft (43.2%) pulping processes with Arundo as the raw material.

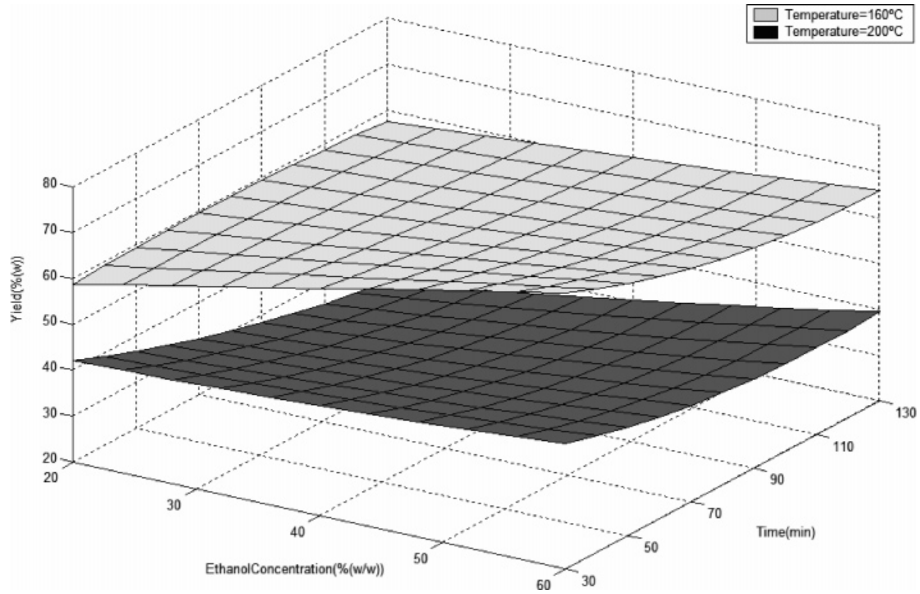

**Figure 3.** Variation of yield as a function of time and ethanol concentration at two pulping temperature levels.

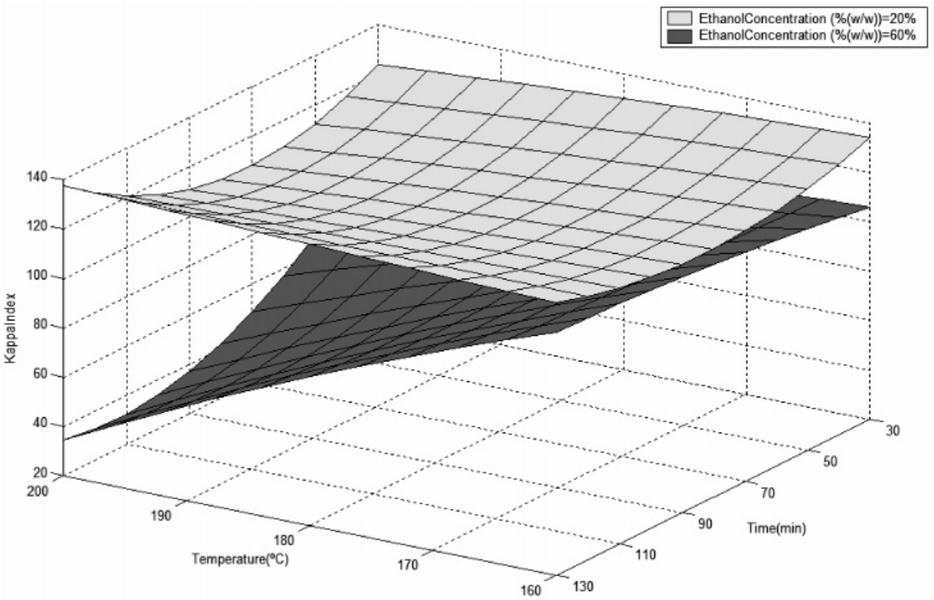

**Figure 4.** Variation of the kappa index as a function of temperature and time at two ethanol concentration levels.

As can be seen from Figure 3, the kappa index was thus much more sensitive to changes in the ethanol concentration than to changes in other independent variables. A negative influence (better kappa index) of almost all the independent variables has been found. Then, to produce pulps with a low kappa index, it is advisable to use a high ethanol concentration, high pulping temperature, and long pulping time. In this case, the influence of a short pulping time and low ethanol concentration on the kappa index variation has been found at a low pulping temperature.

The main parameter influencing viscosity variation is the pulping temperature. As can be seen in Figure 4, at lower values of ethanol concentration, a low influence of temperature and pulping time have been found. That is to say, at low ethanol concentrations, the viscosity values obtained are independent of pulping temperature and time. When using a high ethanol concentration, an increase in the viscosity values of high-pulping-temperature and long-pulping-time pulps have been found. The viscosity values are higher at high values of the pulping temperature, ethanol concentration, and long pulping time. It could be due to high-intensity pulping conditions (among studied); most of the hemicelluloses could be dissolved, but lower cellulose depolymerization could take place. It could be due to the inhibition of intermolecular cellulose chain scission reactions[53] by the ethanol. Then, at high pulping temperatures values, the viscosity of pulps builds up in direct proportion to the organic solvent.

Glucan shows the very important influence of pulping temperature (Figure 5). The ethanol terms present a negative influence for the values of glucan, and then, the production of a relatively high glucan pulp is favored by low ethanol concentration in the pulping liquor. In that case, high values in the pulping temperature and pulping time and low values in the ethanol concentration ensure, in the range considered, the optimum values of glucan. However, high depolimerization (low viscosity values) has been found under those conditions.Comparative characteristics for Arundo under ethanol soda,[52] organosolv (without hydrothermal pretreatment), and organosolv optimum conditions (with hydrothermal pretreatment) have been studied (Table 8).

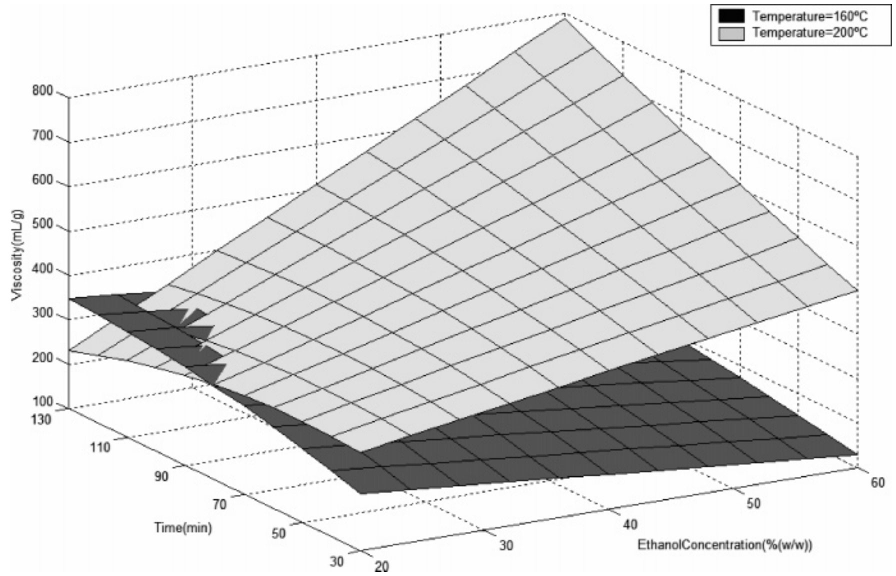

**Figure 5.** Variation of viscosity as a function of ethanol concentration and time at two pulping temperature levels.

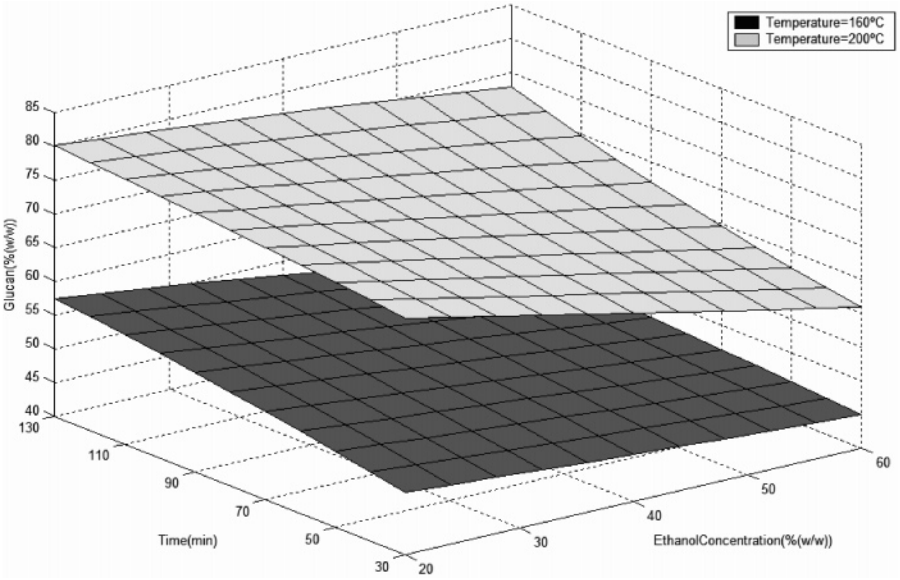

**Figure 6.** Variation of glucan content as a function of ethanol concentration and time at two pulping temperature levels.

**Table 8. Properties of Arundo Pulps**

| | initial raw material (nonhydrothermal treatment) | | | | solid phase after autohydrolysis (optimum conditions) | |
|---|---|---|---|---|---|---|
| pulp property (% on oven-dry basis) | ethanol soda[49] | organosolv (1,1,1)[a] | organosolv (0,0,0)[b] | organosolv (−1,−1,−1)[c] | organosolv (1,1,1) | organosolv (1,1,1)[d] |
| yield (%) | 46.80 | 38.24 | 43.16 | 66.35 | 41.36 | 35.24 |
| kappa index | | 53.50 | 86.18 | | 38.75 | 38.75 |
| glucan (%) | | 68.5 | 59.59 | 42.43 | 71.05 | 60.5 |
| holocellulose (%) | | 77.71 | 75.91 | 66.39 | 84.63 | 72.10 |
| lignin (%) | 4.04 | 12.11 | 20.32 | 22.44 | 8.68 | 7.39 |
| remove lignin (%)[d] | 90.3 | 80.0 | 62.4 | 35.4 | 88.3 | 88.3 |
| xylan (%) | 22.53 | 8.76 | 14.96 | 20.86 | 12.89 | 10.98 |
| acetil groups (%) | | 0.45 | 1.36 | 3.1 | 0.69 | 0.59 |
| viscosity (mL/g) | 1146 | 870.7 | 400.0 | 134.7 | 729.3 | 729.3 |

[a] 60% of ethanol concentration, 200 °C, and 130 min. [b] 40% of ethanol concentration, 180 °C, and 80 min. [c] 20% of ethanol concentration, 160 °C, and 30 min. [d] Percentages with respect to initial raw material content.

In that table, similar values for yield and glucan content have been found in the pulp after autohydrolysis with respect to similar conditions and initial raw material. However, lower kappa index and lignin values have been found under those conditions. Also, with respect to low-intensity pulping conditions (0, 0, 0) and (−1, −1, −1), lower values for the evaluated parameters have been obtained, except that the yield that has increased.

A comparative study of organosolv conditions under hydrothermal treatment with respect to ethanol soda Arundo pulping[52] has been done. Higher yield and lower lignin content have been found. However, similar lignin content has been removed for both processes. Also, higher hemicellulose (xylan) content has been found for ethanol soda pulping. Then, a higher xylan content is expected to be removed in the present study and a more efficient subsequent bleaching could be performed.[51] In that study, it is shown that viscosity values are higher in the ethanol soda pulping process and organosolv in the initial raw material than in organosolv hydrothermal treatment; however, the properties of both organosolv pulps are quite similar.

## 4. Conclusions

Ethanol−water pulping could be an adequate process for obtaining solid residues from the authohydrolysis of *Arundo donax* L.

From autohydrolysis, a valuable liquid phase could be obtained. In that phase, a greater increment in the content of xylooligomers has been found from 185 to 200 °C. Nevertheless, maximum glucose and xylose contents have been obtained at 180°C.

Pulping temperature has a great influence on the highest number of the dependent variables except for the kappa index. An increment in pulping temperature has a positive effect on the kappa index, viscosity values, and glucan content. However, it has a negative effect on the yield.

Suitable characteristics of pulps and acceptable yield, viscosity, and kappa index values could be obtained by operating at high temperature (200 °C), pulping time (130 min), and ethanol concentration (60%). The yield and kappa index values found for pulps from solid residues of *Arundo donax* L. autohydrolysis were similar to those found for other *Arundo donax* L. pulps.

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# Optimizing Cellulosic Paper Obtained from *Arundo Donax L.* under Hydrothermal Treatment

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**Abstract:** This paper deals with the study of the autohydrolysis treatment of *Arundo Donax L* to obtain a valuable liquid phase and a suitable solid residue for papermaking. The influence of operational conditions in the organosolv pulping (viz., ethanol concentration, temperature and pulping time) on the yield and physical properties of the paper sheets is studied to determine the best pulping conditions to provide suitable paper quality. Moreover, a refining process was used to increase the quality of paper sheets. Maximum temperature of 185 °C was achieved in the autohydrolysis of the raw material in order to ensure a minimum degradation of cellulose fiber, suitable removal of the extractives compounds which could be source of further problems related to pitch, and extraction of part of the hemicellulosic fraction (olygomers and some monomers). Temperature displays great positive influence on the highest number of dependent variables. In that form, suitable physical properties of paper sheets were obtained by operating at high temperature (200 °C) and ethanol concentration (60 %) and long pulping time (130 min). Under these conditions, paper with 17 kN m $kg^{-1}$ for tensile index, 0.58 kPa $m^2$ $g^{-1}$ for burst index and 0.95 kN $m^2$ $g^{-1}$ for tear index could be obtained. Refining process increases the physical properties of paper sheets in: 125.9 % - tensile index, 113.6 % - burst index and 39.8 % - tear index.

***Keywords:*** *Arundo donax, ethanol pulping, hydrothermal treatment, cellulose paper, autohydrolysis*

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## Introduction

Nowadays, there is a trend for fine papermaking using short fibers rather than cut long fibers and the development of those fibers [1]. In this sense, the use of nonwoody faster growing species for papermaking could report several advantages because they provide remediation for the environmental problems associated to the use of those vegetable species.

With this perspective, *Arundo Donax* L. is a stout perennial grass, with thick, short, branched rhizomes. It could culm up to 6 m tall, with a rapid growth rate and a strong vegetative competitive ability which enable it to that industrial use. Its cane could be used for biomass for energy [2], and its stems are harvested for use in papermaking and other industrial uses [3].

*Arundo Donax* L. is reported to tolerate annual precipitation of 3～40 dm, an annual temperature of 9～28 °C, and a pH of 5.0～8.7 [4]. Duke [5] cites evidence that its annual productivity ranges from 10～59 Mt $ha^{-1}$, and according to Westlake [6], *Arundo Donax* L. could produce 40～75 Mt (hayear) $^{-1}$ in warm temperature and tropical regions.

On the other hand, there is an increasing interest in applying new environmental friendly technologies to refine lignocellulosic material, such as autohydrolysis [7]. Autohydrolysis processes are based on the utilization of water as the sole fractionation agent to extract from these materials a liquid mixture enriched of olygomers and some monomers, such as glucose, mannose, galactose, arabinose, xylose etc, which could be used as commercial source of organic reagents [8]. Moreover, the solid fraction of this treatment could be used as raw material for alcohol production [9], ruminant feed [10] etc. In this way, an interesting alternative is its use as raw material for pulp and papermaking [11]. Additionally, the autohydrolysis process could remove the extractable com-

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pounds which compose the raw material [12]. These compounds could cause problems related to pitch. Pitch deposits during papermaking represent a complex phenomenon with an increasing incidence during last years [13,14]. Pitch can cause problems by adhering to machinery and reducing the quality of pulp then.

The cellulose pulping processes based on sulphur free organic solvent could be considered as an interesting alternative to kraft and sulphite processes because of the use of lower polluting and easily recoverable reagents such as organic dissolvents [15]. In this way, organosolv pulping minimizes problems related to sulphur emissions, and it has been found to be effective on several wood species, with a broad range of organic dissolvents [16]. However, papers produced from organosolv pulping are suitable for uses where strengh is not the most important property since fibers thus produced are weaker than those produced by kraft processes [17]. In this sense, a great amount of organic dissovents has been used, with addition of catalyst or without it (acids, bases and salts) [18]. Ethanol is one of the most promising dissolvents because of its high power for dissolving lignin and its easy recovery too [19].

An integrated, value-added management plan involves the optimum use of all wood compounds to reach maxima valorization. If more than one valorization technique is used, these ones should be compatible with one another. In this way, an autohydrolysis treatment and the subsequent pulping process could be an effective, economical, environmentally friendly value-added strategy.

This paper deals with the study of an autohydrolysis treatment to obtain valuable liquid phase and suitable solid residue for papermaking from *Arundo Donax* L. The influence of operational conditions in the organosolv pulping (viz., ethanol concentration, temperature and pulping time) on the yield, tensile index, burst index, tear index, and brightness is studied to determine the best pulping conditions to provide appropriate paper quality, under ANFIS (Adaptative Neural Fuzzy Inference System) mathematical modelling.

## Experimental

### Characterization of the Raw Material

*Arundo donax* L wood trimmings samples were milled to pass a 8 mm screen, since no diffusional limitations were observed for this particle size in preliminary studies. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored. Aliquots from the homogenized wood lot were subjected to moisture determination (drying at 105 $^{o}$C to constant weight), quantitative acid hydrolysis with 5 mL of 72 % sulfuric acid for an hour and quantitative posthydrolysis with 4 % $H_2SO_4$ (adding water until 148.67 g) at 121 $^{o}$C during 60 min. Before HPLC analysis, the solid residue from posthydrolysis stage was recovered by filtration and considered as Klason lignin, sugar degradation and acid soluble lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar decomposition) the contents of samples in cellulose (as glucan), hemicelluloses (xylan, araban, uronic acids), and acetyl groups. The moisture of wood was considered as water in the material balances. In that form, $\alpha$-cellulose is glucan and holocellulose includes glucan, xylan, araban and uronic acids. Chromatographic separation was performed using an ion-exchange resin Metacarb 87 H column (300 × 7.8 mm, Varian, USA) under the following conditions: mobile phase 0.05 mol $L^{-1}$ sulfuric acid, flow rate 0.5 mL min.$^{-1}$, column temperature 30 $^{o}$C. The volume injected was 20 μL.

Characterization of raw material includes the content of uronic acids [20], ethanol extractives (Standard Tappi 204) and ashes (Standard Tappi 211).

Characterization experiments of pulps and paper sheets involved the following parameters: pulp yield (Standard Tappi 257), viscosity (UNE 57039), brightness (Standard Tappi 525), tensile index (UNE 57054), burst index (UNE 57058), and tear index (UNE 57-033-86).

Additionally, in order to improve the quality of paper sheets, pulp in optimum conditions were subjected to a refining process in a Valley beater (ISO 5264/1).

### Hydrothermal Pretreatment Procedure

Wood chips and water were mixed in the desired proportions (1:8) and reacted in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated (from 150 to 200 $^{o}$C, Table 3) with external mantles. In Figure 1 the temperature profile during the heating process of the reactor has been shown. The reaction media were heated during the desired time, depending on the required temperature (Figure 1), and then cooled. After achieving normal pressure (monitored by barometer implemented in the reactor), the reactor was opened and samples of the suspensions were withdrawn. The solid/liquid ratio was fixed (1/8) and held constant in all experiments. This value is, among practiced values, the minimum value that allows a homogeneous mixture. At the end of treatment, the solid residues were recovered by filtration and washed with distilled water. A fraction was used for pulping and another fraction was air-dried and milled to a particle size <0.5 mm. Milled samples were assayed for cellulose, hemicellulose, lignin and acetyl groups using the same methods as for raw material analysis. An aliquot of liquors was filtered through 0.45 μm membranes and used for di-

**Table 1.** Chemical Composition of Arundo and other Pulp Raw Materials

| % oven dry matter basis[a] | Present study | Arundo Donax [28] | Kenaf [29] | Aspen [30] | E.G [11] | EG [31] |
|---|---|---|---|---|---|---|
| Ash | 3.0 (0.3) | n.d | n.d | n.d | 1.2 | n.d. |
| EtOH extractives | 9.1 (1.4) | n.d | n.d | n.d | 0.6 | 1.72 |
| Glucan | 34.8 (5.6) | 30.5 | 40 | 36.3 | 46.8 | 53.4 |
| Xylan | 19.4 (2.3) | 8.10 | 19 | 22.7 | 16.6 | 14.2 |
| Araban | 1.5 (0.0) | 0.62 | 1.8 | 0.6 | 0.54 | 0.4 |
| Acetyl groups | 3.4 (0.2) | n.d | n.d | n.d | 3.56 | n.d. |
| Uronics Acids | 5.5 (0.3) | n.d | n.d | n.d | n.d. | n.d. |
| Klason Lignin | 23.0 (0.5) | 15.8～22.0 | 13.4 | 19.3 | 22.9 | n.d |

[a] Standard deviations are shown within parenthesis.

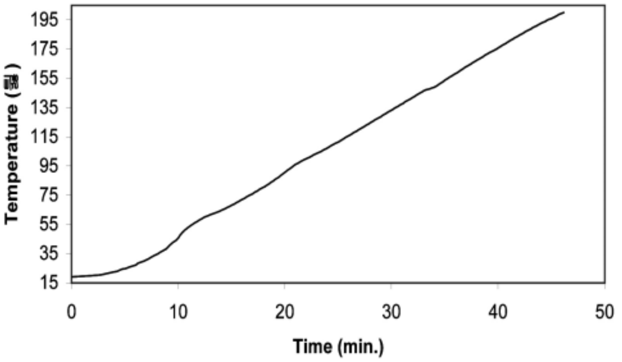

**Figure 1.** Temperature profile in reactor during the heating process.

rect HPLC determination of monosaccharides, furfural and acetic acid. A second aliquot of liquors (25 mL) was subjected to quantitative posthydrolysis (with 4 % $H_2SO_4$ at 121 $^{o}$C during 60 min) before HPLC analysis. For understanding the increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis, the concentrations of oligomers [21] and acetyl groups bound to oligosaccharides were measured.

### Pulping Procedure

Cellulose pulps were obtained in the same reactor used in the autohydrolysis pre-treatment. The initial liquor to solid ratio was 8:1 (dry wt. basis), the ethanol concentration in the cooking liquor range from 20, 40, and 60 % by weight, temperature from 160, 170, 180, 190, and 200 $^{o}$C and pulping time from 30, 55, 80, 105, and 130 min. The reactor was then closed and simultaneously heated and actuated to assure good mixing and uniform swelling of *Arundo donax* L.

After finishing the pulping time, the reactor is cooled and the controller temperature is then set to 25 $^{o}$C.

Following cooking, the pulp was separated from the liquor and disintegrated, without disturbing the fibers, during 3 min, washed on a sieve of 0.16 mm mesh, defibered and passed through a Strainer filter (0.4 mm mesh) in order to isolate the uncooked material.

### Statistical Analysis by Adaptative Neural Fuzzy Inference System (ANFIS)

ANFIS modelling, proposed by Jang [22] and based on the first order Sugeno-fuzzy modelling has been successfully applied to the simulation and control of several processes [23-26]. In that form, the ANFIS paradigm used is a multilayer feed forward back-propagation network. An adaptive network that is functionally equivalent to a Sugeno fuzzy model has been constructed. The adaptive network can tune the fuzzy system with a back-propagation algorithm based on the collection of input-output data. This provides fuzzy system the ability to learn. The detailed architecture and learning procedure for ANFIS can be found in related literature [27].

The mathematical equation which responses to different rules is:

$$y_e = \frac{\sum_{i=1}^{m} y_l \cdot R_l}{\sum_{i=1}^{m} R_l} \qquad \text{(Eq. 1)}$$

$y_e$= estimate value of output variable,
$m$= number of rules,
$y_l$= defuzzifier.
$R_l$ = the product of the selected membership functions.

The parameters and constants in the previous equation were estimated by using the ANFIS tool in the Matlab software suite.

## Results and Discussion

### Raw Material Characteristics

*Arundo donax* L. (Arundo) raw material samples were taken from La Rábida (Huelva). In Table 1 [11,28-31], a comparison of glucan, xylan, araban, acetyl groups, ethanol extractives, and ashes has been made in regard to *Eucalyptus globulus* (EG), which was used as reference, and other raw materials. Arundo composition is similar to that found by Shatalov [28]. However, certain variation has been observed in that table since uncontrollable

**Table 2.** Fractionation and Composition of Solid Residue and Liquid Phase after Autohydrolysis Treatment at 185 ºC

| | | |
|---|---|---|
| Solid yield (%) | | 83.54 |
| Non volatile solids content (%) | | 12.48 |
| Volatile solids content (%) | | 3.99 |
| Composition of solid residue (%)[a] | Glucan | 38.09 |
| | Xylan | 20.62 |
| | Araban | 0.91 |
| | Acetyl groups | 3.65 |
| | Lignin | 26.58 |
| Composition of liquid phase (%)[b] | Glucose | 0.89 |
| | Xylose | 0.73 |
| | Arabinose | 0.15 |
| | Acetic acid | 1.26 |
| | HMF[c] | 0.09 |
| | Furfural | 0.24 |
| | Olygomers | 2.41 |

[a]Percentages oven dry matter basis
[b]Percentages of extraction with respect to initial raw material
[c]5-hydroxymethylfurfural.

factors such as weather and water availability play a significant role in controlling the measured properties.

In regard to EG, lower contents of glucan, slightly higher content of hemicellulose (xylan, araban and acetyl groups), higher contents of ethanol extractives and similar contents of lignin and ash have been found. The high content of ethanol extractives could cause problems related to pitch [13,14], A prior autohydrolysis treatment to pulping process then could remove these compounds and increase the quality of pulp and paper sheets.

Additionally, a comparison in regard to other alternative cellulose pulp raw materials (Kenaf and Aspen) has been made. Similar contents of glucan, xylan and araban have been found. However, the lignin content is higher for Arundo.

Arundo then could be a suitable raw material for the autohydrolysis treatment to extract valuable products (olygomers and some monomers) and minimize pitch deposits to optimize the further pulping process. Nevertheless, Arundo could obtain a lower pulping yield because of the high lignin and ethanol extractives contents in regard to EG wood and other raw materials.

## Autohydrolysis Treatment

Based on previous experiences [11], a non isothermal autohydrolysis of Arundo was studied to obtain a significant extraction of several compounds together with minimum degradation of pulp. Maximum temperature of 185 ºC (Figure 1) then was selected. Higher temperatures could degradate the cellulosic fibers and reduce the viscosity values [32,33] of pulps and its quality then could be reduced.

In Table 2, the fractionation (yield, volatile and non volatile compounds) and the composition of solid and liquid phases obtained after the autohydrolysis treatment is displayed. Olygomers are generated via hydrolysis of the hemicellulosic fraction [34], and are the most extracted compound of the liquid phase (2.41 %). The extraction of monomers (glucose, xylose, arabinose, and acetyl groups) and degradation products (5-hydroximethylfurfural and furfural) means about 3.36 %. A value of 5.57 % in regard to initial raw material then was extracted. The volatile and non volatile content is 16.47 %, which means that 10.7 % of the extracted compounds does not compose the cellulose or hemicellulosic fraction. This fraction stems from the ethanol extractives compounds of the raw material (9.1 %) and can't be analyzed by HPLC.

Additionally, chemical characterization of solid phase obtained at 185 ºC is also shown in Table 2. A comparison of the solid phase obtained under this process in regard to the raw material (Tables 1 and 2) let us know that lignin, cellulose and hemicelluloses percentages (xylan and acetyl groups) are similar. Slight increments were found in those contents, justified by a concentration effect.

## Optimization Studies in Pulping Procedure

The solid obtained after autohydrolysis treatment was used for pulping process.

In Table 3 the standardized values of the independent variables and the properties of the obtained cellulose pulps and paper sheets according to the proposed experimental design were shown. Each of the experimental results (viscosity and physical properties of paper sheets) is an average value of at least 5 determinations. The deviations of each one of those parameters with respect to their averages are smaller than 5 % in all the cases.

The values of the independent variables of the factorial design proposed have been estimated on the basis of literature and experience [35,36]. In that form, the values fixed for temperature are -1 (160 ºC), -0.5 (170 ºC), 0 (180 ºC), 0.5 (190 ºC), and 1 (200 ºC); for time -1 (30 min), -0.5 (55 min), 0 (80 min), 0.5 (105 min), and 1 (130 min); and for ethanol concentration -1 (20 %), 0 (40 %) and 1 (60 %).

According to ANFIS analysis for each dependent variable (Table 3) as a function of the independent variables, the mathematical models are shown in Table 4.

For this study, the optimum number of rules has been selected at 8 (Table 5), developing then eq. 1:

$$y_e = \frac{y_1 \cdot R_1 + y_2 \cdot R_2 + y_3 \cdot R_3 + y_4 \cdot R_4 + y_5 \cdot R_5 + y_6 \cdot R_6 + y_7 \cdot R_7 + y_8 \cdot R_8}{R_1 + R_2 + R_3 + R_4 + R_5 + R_6 + R_7 + R_8} \qquad \text{(Eq. 2)}$$

**Table 3.** Values of Independent Variables and Properties of the Pulp Obtained in the Organosolv Pulping Process Using the Proposed Experimental Design

| Normalized values of ethanol conc., temperature and time | | | Yield (%) | Tensile index (kN m $kg^{-1}$) | Burst index (kPa · $m^2$ $g^{-1}$) | Tear index (kN · $m^2$ $g^{-1}$) | Brightness (%ISO) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 41.36 | 12.18 | 0.48 | 0.81 | 18.0 |
| -1 | 1 | 1 | 23.52 | 2.70 | 0.29 | 0.30 | 14.3 |
| -1 | -1 | 1 | 56.76 | 6.80 | 0.18 | 0.40 | 13.4 |
| 1 | -1 | 1 | 68.48 | 5.50 | 0.20 | 0.49 | 17.3 |
| 0 | 0 | 1 | 49.52 | 8.70 | 0.35 | 0.58 | 16.3 |
| 1 | 1 | -1 | 48.88 | 11.77 | 0.53 | 0.79 | 16.6 |
| -1 | 1 | -1 | 44.35 | 2.97 | 0.13 | 0.35 | 14.6 |
| -1 | -1 | -1 | 56.72 | 3.95 | 0.19 | 0.14 | 15.0 |
| 1 | -1 | -1 | 79.67 | 2.57 | 0.10 | 0.31 | 17.0 |
| 0 | 0 | -1 | 57.42 | 5.86 | 0.30 | 0.42 | 16.4 |
| 0 | 0 | 0 | 45.66 | 9.80 | 0.29 | 0.62 | 16.7 |
| 1 | 0 | 0 | 54.91 | 10.26 | 0.32 | 0.58 | 16.1 |
| 0 | 1 | 0 | 35.23 | 10.60 | 0.41 | 0.61 | 17.0 |
| -1 | 0 | 0 | 49.53 | 5.97 | 0.14 | 0.33 | 15.0 |
| 0 | -1 | 0 | 67.78 | 5.94 | 0.16 | 0.33 | 16.7 |
| 0 | 0 | 0.5 | 50.59 | 9.39 | 0.29 | 0.55 | 16.5 |
| 1 | 0 | 0.5 | 52.89 | 11.30 | 0.38 | 0.70 | 18.0 |
| 0 | 1 | 0.5 | 30.24 | 9.53 | 0.46 | 0.58 | 17.5 |
| -1 | 0 | 0.5 | 47.59 | 7.10 | 0.17 | 0.42 | 14.1 |
| 0 | -1 | 0.5 | 65.56 | 7.85 | 0.16 | 0.42 | 15.7 |
| 0 | 0 | -0.5 | 51.61 | 9.42 | 0.31 | 0.52 | 15.5 |
| 1 | 0 | -0.5 | 63.77 | 9.55 | 0.33 | 0.54 | 16.3 |
| 0 | 1 | -0.5 | 38.13 | 10.24 | 0.41 | 0.60 | 16.8 |
| -1 | 0 | -0.5 | 46.97 | 5.01 | 0.14 | 0.36 | 15.0 |
| 0 | -1 | -0.5 | 68.70 | 5.20 | 0.13 | 0.27 | 16.7 |
| 0 | 0.5 | 0 | 42.34 | 10.88 | 0.38 | 0.63 | 17.0 |
| 1 | 0.5 | 0 | 53.45 | 12.40 | 0.45 | 0.80 | 16.0 |
| 0 | 0.5 | 1 | 42.29 | 8.53 | 0.36 | 0.61 | 17.7 |
| -1 | 0.5 | 0 | 38.39 | 4.91 | 0.15 | 0.40 | 14.6 |
| 0 | 0.5 | -1 | 50.15 | 8.30 | 0.30 | 0.65 | 15.5 |
| 0 | -0.5 | 0 | 57.51 | 7.86 | 0.23 | 0.45 | 16.0 |
| 1 | -0.5 | 0 | 59.79 | 7.10 | 0.19 | 0.48 | 17.1 |
| 0 | -0.5 | 1 | 50.29 | 8.98 | 0.32 | 0.63 | 15.6 |
| -1 | -0.5 | 0 | 55.05 | 7.88 | 0.15 | 0.42 | 14.4 |
| 0 | -0.5 | -1 | 72.61 | 4.75 | 0.21 | 0.32 | 17.1 |

Where non normalized values of ethanol concentration are (-1 (20 %), 0 (40 %), 1 (60 %)), temperature (-1 (160 ºC),-0.5 (170 ºC), 0 (180 ºC), 0.5 (190 ºC), 1 (200 ºC)), and time (-1 (30 min), -0.5 (55 min) 0 (80 min), 0.5 (105 min), 1 (130 min))

Additionally, a defuzzifier based on the first-order Suggeno fuzzy model has been chosen. The mathematical equation which response to this defuzzifier is:

$$y_l = a_l \cdot c + b_l \cdot T + c_l \cdot t + d_l \qquad \text{(Eq. 3)}$$

Where $a_l$; $b_l$; $c_l$, and $d_l$ are the estimated parameters to minimize the error, whereas c is the ethanol concentration, T is the temperature and t is the pulping time. In addendum, linear membership functions have been selected, with 2 functions per independent variable, one representing low values and the other one representing high values. The two membership functions for each independent parameter are:

$$P_1 = 1 - \frac{1}{P_{\max} - P_{\min}} \cdot (P - P_{\min}) \qquad \text{(low)} \qquad \text{(Eq. 4)}$$

$$P_2 = 1 - \frac{1}{P_{\max} - P_{\min}} \cdot (P - P_{\min}) \qquad \text{(high)} \qquad \text{(Eq. 5)}$$

where $P_i$ is the membership function and it could be replaced by:

**Table 4.** Parameters, for each One of the Dependent Variables, of the Polynomials Mathematical Models Obtained by ANFIS Analysis on the Proposed Experimental Design

| | | | | |
|---|---|---|---|---|
| | Tensile index (kN m kg$^{-1}$) ($r^2$=0.979) | | | |
| 1 | 0.0083 | 0.01505 | 0.04795 | -4E-05 |
| 2 | 0.04172 | 0.06377 | -0.0283 | 1.61E-04 |
| 3 | 0.04446 | 0.00445 | 0.05432 | 1.3E-04 |
| 4 | 0.04241 | 0.01929 | -0.0132 | 2.87E-04 |
| 5 | -0.015 | 0.0168 | 0.02531 | -9.8E-05 |
| 6 | -0.0326 | 0.06102 | -0.0159 | 9.96E-05 |
| 7 | -0.0162 | 0.05317 | 0.1003 | 4.28E-04 |
| 8 | -0.0014 | 0.07257 | -0.0109 | 5.89E-04 |
| | Burst index (kPa・m$^2$ g$^{-1}$) ($r^2$=0.988) | | | |
| 1 | 0.000986 | 0.0013 | -0.00125 | 8.44E-06 |
| 2 | 0.001409 | -0.00021 | 0.001497 | -5.7E-08 |
| 3 | 0.001808 | 0.000537 | -0.00024 | 2.44E-06 |
| 4 | 0.001912 | 0.000842 | 0.000726 | 3.21E-06 |
| 5 | -0.00069 | 0.000996 | -0.00051 | 2.17E-06 |
| 6 | -0.00128 | 0.001244 | 0.000845 | 2.1E-06 |
| 7 | -0.00078 | 0.002622 | 0.002518 | 1.64E-05 |
| 8 | -0.00079 | 0.002628 | 0.000271 | 1.77E-05 |
| | Tear index (kN・m$^2$ g$^{-1}$) ($r^2$=0.965) | | | |
| 1 | 0.000352 | 0.000611 | 0.001105 | -2.3E-05 |
| 2 | 0.000938 | 0.002636 | 0.000261 | 1.1E-05 |
| 3 | 0.001256 | 0.001631 | 0.001521 | 1.3E-05 |
| 4 | 0.000854 | 0.001395 | 0.000342 | 1.13E-05 |
| 5 | 9.07E-05 | 0.001782 | 0.000363 | 8.12E-06 |
| 6 | -0.00011 | 0.00248 | 0.00119 | 1.01E-05 |
| 7 | 0.00035 | 0.003854 | 0.00184 | 2.17E-05 |
| 8 | 0.000591 | 0.003194 | 0.001451 | 2.03E-05 |
| | Brightness (% ISO) ($r^2$=0.930) | | | |
| 1 | 0.02501 | 0.08737 | 0.03223 | 0.000525 |
| 2 | 0.01723 | 0.05893 | 0.02856 | 0.000347 |
| 3 | 0.01932 | 0.06797 | 0.03132 | 0.000357 |
| 4 | 0.02402 | 0.05962 | 0.02041 | 0.000316 |
| 5 | 0.02093 | 0.09343 | 0.03046 | 0.000591 |
| 6 | 0.01478 | 0.07011 | 0.0416 | 0.000418 |
| 7 | 0.01027 | 0.07595 | 0.02062 | 0.000374 |
| 8 | 0.003678 | 0.06809 | 0.03697 | 0.000357 |

$C_i$ if the ethanol concentration ($p_{max}$ = 60 % and $p_{min.}$ = 20 %.C ) is used,
by $T_i$ if the temperature ($p_{max}$=200 °C, $p_{min.}$=160 °C) is used
or by $t_i$ if the pulping time ($p_{max}$=130 min and $p_{min.}$=30 min) is used.

$R_l$ is defined by the product of three membership functions (one per independent variable), the selected combinations of membership functions are:

$$R_1 = C_1 \cdot T_1 \cdot t_1 \qquad \text{(Eq. 6)}$$

**Table 5.** Selected Rules and Their Respective Linguistic Values

| Rules | Ethanol concentration | Temperature | Time |
|---|---|---|---|
| 1 | Low | Low | Low |
| 2 | Low | Low | High |
| 3 | Low | High | Low |
| 4 | Low | High | High |
| 5 | High | Low | Low |
| 6 | High | Low | High |
| 7 | High | High | Low |
| 8 | High | High | High |

$$R_2 = C_1 \cdot T_1 \cdot t_2 \qquad \text{(Eq. 7)}$$

$$R_3 = C_1 \cdot T_2 \cdot t_1 \qquad \text{(Eq. 8)}$$

$$R_4 = C_1 \cdot T_2 \cdot t_2 \qquad \text{(Eq. 9)}$$

$$R_5 = C_2 \cdot T_1 \cdot t_1 \qquad \text{(Eq. 10)}$$

$$R_6 = C_2 \cdot T_1 \cdot t_2 \qquad \text{(Eq. 11)}$$

$$R_7 = C_2 \cdot T_2 \cdot t_1 \qquad \text{(Eq. 12)}$$

$$R_8 = C_2 \cdot T_2 \cdot t_2 \qquad \text{(Eq. 13)}$$

Consequently, $y_l$ represents the linear behavior of the system in the conditions of ethanol concentration, temperature and pulping time defined by $R_l$.

According to Tables 4 and 5, pulping temperature is the most strongly influential variable on yield pulp because of the hydrolysis of residual lignin and hemicellulose bonds [36,37]. The highest yield (79.6 % in regard to material pulping process) is noted at low values of pulping temperature, low values of time and high ethanol concentration.

The response surfaces for each dependent variable were plotted at maxima and minima levels of the most strongly independent variable (Figures 2～6) in order to determine the values of the independent variables giving the optimum tensile index, burst index, tear index and brightness.

According to Figure 2 (tensile index), 3 (burst index), and 4 (tear index), a similar evolution of such physical properties is observed. The temperature displays a positive influence. However, at low ethanol concentrations, physical properties are similar at low and high temperatures. A positive influence has been found for ethanol concentration at high temperatures, and a slight influence at low temperatures. In addendum, pulping time displays a slight influence in those properties. The highest values of physical properties then are found at high temperatures and ethanol concentration.

In Figure 5, the variation of brightness at two different

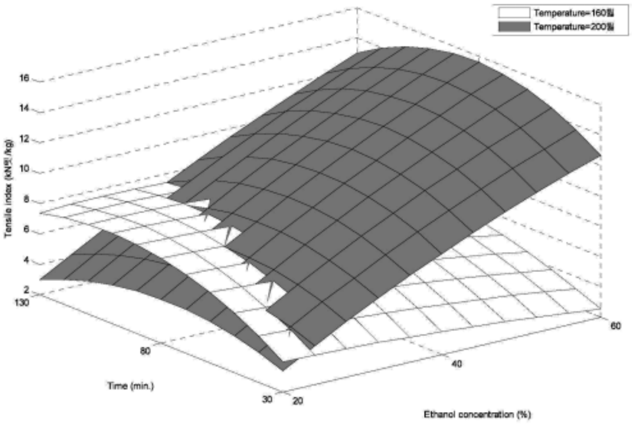

**Figure 2.** Variation of tensile index as a function of time and ethanol concentration at two pulping temperature levels.

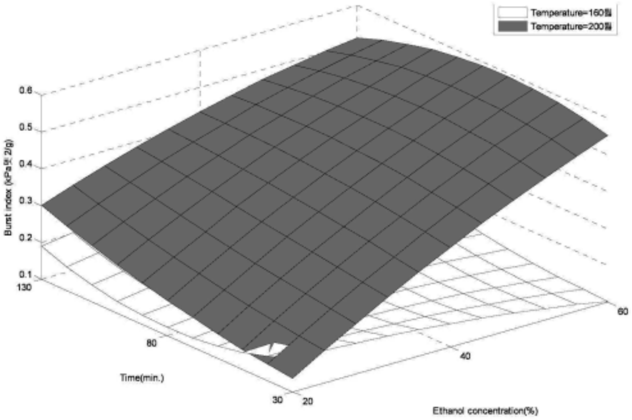

**Figure 3.** Variation of burst index as a function of time and ethanol concentration at two pulping temperature levels.

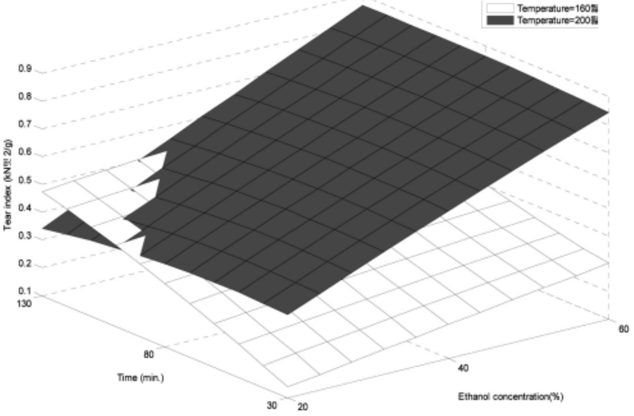

**Figure 4.** Variation of tear index as a function of time and ethanol concentration at two pulping temperature levels.

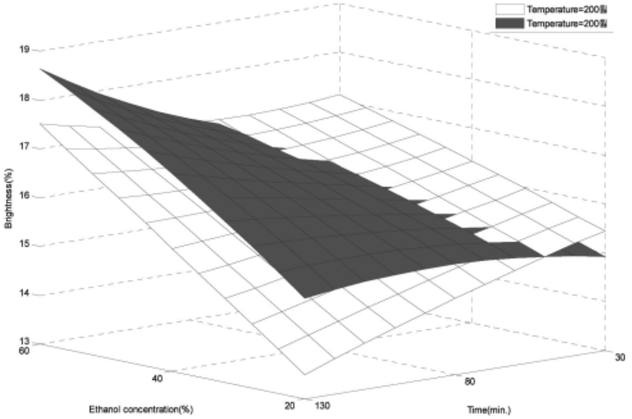

**Figure 5.** Variation of brightness as a function of time and ethanol concentration at two pulping temperature levels.

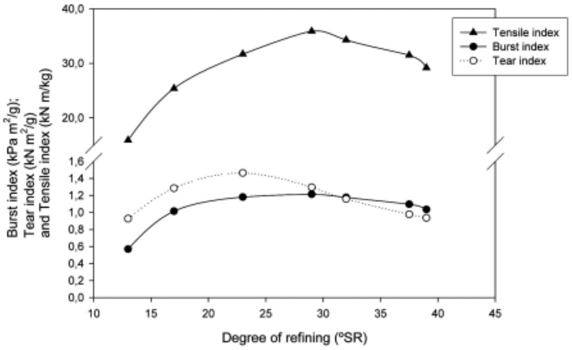

**Figure 6.** Variation of tensile index, burst index and tear index as a function of Shopper Riegler.

pulping temperatures is shown. A negative influence of ethanol concentration is found. Moreover, negative influence of pulping time is found at low temperatures, and positive influence at high temperatures. At high temperatures, brightness is higher at long pulping time than short's. The highest brightness values then are obtained at high temperatures, high ethanol concentration and long pulping time.

In Table 6, a comparison of physical properties between papers sheets with autohydrolysis treatment and without's, under the same pulping conditions, is shown. According to that table, viscosity of pulps is higher without autohydrolysis treatment; physical properties then are slight higher without autohydrolysis treatments. This could be justified by the depolymerization which takes place under this treatment, which could reduce the viscosity values and the quality of the obtained paper sheets. However, autohydrolysis treatments could reduce problems related to pitchs.

To study the evolution of physical properties, pulps obtained under optimum conditions without autohydrolysis treatment were subjected to a refining process, in a standard Valley beating run (according to Tappi Standard T 200 sp-96). In Figure 6, the evolution of these properties is shown. Maximum tensile index and burst index values (3.59 km and 1.21 kP · am$^2$ g$^{-1}$, respectively) are found at 29 $^{o}$SR. These values mean an increasing of 125.9 and 113.6 % in regard their initial values. Maximum tear index value (1.46 kN · m$^2$ g$^{-1}$) has been found at 23 $^{o}$SR,

**Table 6.** Comparison Between Pulps and Paper Sheets with and Without Autohydrolyisis Treatment

| | | | pulps and paper sheets without autohydrolysis treatment | | | | pulps and paper sheets with autohydrolysis treatment | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Normalized values of ethanol conc., temperature and time | | | Viscosity ($mL\ g^{-1}$)[a] | Tensile index ($kN\ m\ kg^{-1}$)[a] | Burst index ($kPa \cdot m^2\ g^{-1}$)[a] | Tear Index ($kN \cdot m^2\ g^{-1}$)[a] | Viscosity ($mL\ g^{-1}$)[b] | Tensile index ($kN\ m\ kg^{-1}$)[b] | Burst index ($kPa \cdot m^2\ g^{-1}$)[b] | Tear Index ($kN \cdot m^2\ g^{-1}$)[b] |
| 1 | 1 | 1 | 870.71 | 15.89 | 0.569 | 0.928 | 729.32 | 12.18 | 0.480 | 0.807 |
| 0 | 0 | 0 | 400.05 | 14.76 | 0.481 | 0.951 | 392.25 | 9.80 | 0.290 | 0.620 |
| -1 | -1 | -1 | 210.10 | 4.3 | 0.22 | 0.163 | 186.49 | 3.95 | 0.192 | 0.140 |
| 0 | 0.5 | 0 | 694.91 | 12.10 | 0.427 | 0.858 | 575.20 | 10.88 | 0.385 | 0.630 |
| 0 | -0.5 | 1 | 395.64 | 11.95 | 0.407 | 0.830 | 365.37 | 8.98 | 0.321 | 0.630 |

Where non normalized values of ethanol concentration are (-1 (20 %) , 0 (40 %), 1 (60 %)), temperature (-1 (160 ºC),-0.5 (170 ºC), 0 (180 ºC), 0.5 (190 ºC), 1 (200 ºC)) and time (-1 (30 min), -0.5 (55 min) 0 (80 min), 0.5 (105 min), 1 (130 min)) [a]pulps and paper sheets without autohydrolysis treatment [b]pulps and paper sheets with autohydrolysis treatment

which means 39.8 % in regard to its initial value.

An increase of the different parameters of the paper sheets is observed at increasing the degree of refining. All pulps reached between 33 and 39 $kN\ m\ kg^{-1}$ values in the stretch index and not in excess of the refining degree (< 45 $^{o}$SR). This fact suggests multiplying by a factor between 6 and 2 times approximately in regard to the initial values. For burst index a multiply factor among 3 and 8 was found, reached values between 1.5～2 $kN\ g^{-1}$. The tear index multiplied by 3 approximately, reached values greater than 2.5 $N\ m^2\ g.^{-1}$

A comparison of burst index and tear index, along with the other agricultural residues considered [38,39], reveals the following facts: The burst index for Arundo was higher than those for vine shoots, which revealed a maximum value of 0.99 $kN\ g^{-1}$ at 55SR, similar to those for sunflower stalks (1.62～3.22 $kN\ g^{-1}$) but lower than those for cotton plants stalks (2.09～4.15 $kN\ g^{-1}$) and sorghum stalks (4.2～5.3 $kN\ g^{-1}$). The tear index for olive trimming residues was similar to those for vine shoots (1.50～2.49 $kN\ m^2\ g^{-1}$) and lower than those for sunflower stalks (5.55～6.39 $kN\ m^2\ g^{-1}$), cotton plant stalks (7.02～4.05 $kN\ m^2\ g^{-1}$) and sorghum stalks (5.2～8.5 $kN\ m^2\ g^{-1}$).

## Conclusions

Ethanol-water pulping maybe a suitable process to valorizate the solid residue obtained after an autohydrolysis treatment of *Arundo Donax L.*

Valuable liquid phase could be obtained from autohydrolysis process. In order to ensure a minimum degradation of cellulose fiber a maximum temperature of 185 $^{o}$C was achieved, removing the ethanol extractives compounds from raw material and part of the hemicellulosic fraction (olygomers and some monomers).

Temperature displays great positive influence on the highest number of dependent variables, such as tensile index, tear index and burst index. In that form, suitable viscosity and physical properties of paper sheets were obtained by operating at high temperature (200 $^{o}$C), high ethanol concentration (60 %) and long pulping time (130 min). Under these conditions, paper with 17 $kN\ m\ kg^{-1}$ for tensile index, 0.58 $kPa \cdot m^2\ g^{-1}$ for burst index and 0.95 $kN \cdot m^2\ g^{-1}$ for tear index could be obtained.

Refining process make physical properties of paper sheets increase their values; this increasing is found to be 125.9 % for tensile index, 113.6 % for burst index and 39.8 % for tear index.

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# New perspectives for *Paulownia fortunei* L. valorisation of the autohydrolysis and pulping processes

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**Abstract**

This paper will consider the influence of the temperature of autohydrolysis or hydrothermal process from *Paulownia fortunei* L. to obtain a valuable liquid phase and a suitable solid phase to produce pulp. The solid phase resulting of autohydrolysis was subjected to organosolv pulping process and formed paper sheets, analyzing the influence of operational variables (viz., ethanol concentration, temperature and pulping time) on the yield, viscosity, tensile index, burst index, tear index and brightness.

Maximum glucose and xylose contents and minimum paper sheets characteristic loss have been obtained at 190 °C authohydrolysis temperature. Suitable characteristics of paper sheets and acceptable yield, viscosity and kappa number of pulp could be obtained by operating at 180 °C temperature, 30 min pulping time and 20% ethanol concentration. Under those conditions sheets paper with 27.4% ISO brightness, 28.87 N m/g tensile index, 1.22 kPa m$^2$/g burst index and 1.23 kN m$^2$/g tear index could be obtained.

*Keywords:* *Paulownia fortunei*; Organosolv pulping; Hydrothermal; Pulp; Autohydrolysis

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## 1. Introduction

Paulownia is a tree original of China, where it is well known for more than 2600 years. It could be considered as a low demand water plant, in spite of not growing in barren zones (Jiménez et al., 2005). According to these authors the fiber length is around 0.84 mm, similar to those found for Eucalyptus wood, whose typical values are 0.7–1.3 mm. The content of extractives compounds is 5.46%, higher than those found for Eucalyptus wood, with a value of 2.09% (Jiménez et al., 2005). These compounds could cause problems related to pitch. Pitch deposits in the manufacturing of pulp, represent a complex phenomenon which has increased in recent years (Del Río et al., 2000) and could cause problems by adhering to machinery and reducing the quality of pulp (Gutiérrez et al., 2003). The cellulose content is 37.44%, lower than those found for *Eucalyptus globulus* (52.79%), whereas lignin content is 22.4%, higher than Eucalyptus's one (19.96%) (Jiménez et al., 2005). Nevertheless, Paulownia have an elevated biomass production during its growth phase (Chirko et al., 1996), so in a year it can develop the equivalent to several years of others species, such as wheat straw, sunflower, sorghum, and olive in a year of growth (Jiménez et al., 2002a). Each Paulownia tree could produce a cubic meter of wood at the age of 5–7 years; it may grow in intensive plantations with about 2000 trees by ha. Then, it can be calculated an annual production of 330 ton/ha, nevertheless a more preservative number could be 150 ton/ha (Jiménez et al., 2005).

Moreover, Paulownia can be used for several applications (Curley, 1993; Ede et al., 1997), one of them is its use as source for pulp (Rai et al., 2000). The most suitable variety of Paulownia for this purpose is *Paulownia fortunei* (Rai et al., 2000), characterized by a fast development and an uniform and regular growth (Curley, 1993).

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On the other hand, there is a growing interest in processes to optimize lignocellulosic materials valorisation using environmental-friendly technologies. One of them is autohydrolysis, which is based on the utilization of water as the sole fractionation agent (Vázquez et al., 2005). The autohydrolysis process helps obtain a rich mixture in oligomers and some monomers, such as glucose, mannose, galactose, arabinose and xylose. These compounds could be used as a commercial source of organic reagents (Carvalheiro et al., 2004). In addition, the autohydrolysis process could remove the extractives compounds which are presented in raw material (Caparrós et al., 2006).

The obtained solid fraction from authohydrolysis process, characterized by its high content of lignin and cellulose, could be employed as raw material for alcohol production (Chikako et al., 2005), ruminant feed (Howard et al., 1995), etc. Particularly, an interesting alternative is its use as raw material for pulp and papermaking (Garrote et al., 2003).

Additionally, the pulping processes based on sulphur free organic solvents could be considered as an important alternative to kraft and sulphite processes due to the use of less polluting and easily recoverable organic reagents (McDonough, 1993). Organosolv pulping avoid problems related to sulphur emissions, and it has been found to be effective on several wood species with a broad range of organic solvents, with addition of catalyst or without it (acids, bases or salts); ethanol is one of the most promising solvents due to its high power for dissolving lignin and its easy recovery (Jiménez et al., 1997).

This paper deals with the influence of temperature of the autohydrolysis process on the oligomers and monomer extraction. In addition, the solid phase resulting of such process, will be subjected to pulping process and formed paper sheets, analyzing the influence of operational variables (viz., ethanol concentration, temperature and pulping time) on the yield, viscosity, kappa number, tensile index, burst index, tear index and brightness.

## 2. Experimental

### 2.1. Characterization of the raw material and pulp

*Paulownia fortunei* wood trimmings samples were milled to pass a 8 mm screen. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored. Aliquots from the homogenized wood lot were subjected to moisture determination (drying at 105 °C to constant weight), quantitative acid hydrolysis with 5 ml of 72% sulfuric acid for an hour, and quantitative posthydrolysis with 4% sulfuric acid (adding water until 148.67 g) at 121 °C during 60 min. Before HPLC analysis, the solid residue from posthydrolysis process was recovered by filtration and considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC. The moisture of wood was considered as water in the material balances. Chromatographic separation was performed using an ion-exchange resin Metacarb 87H column (300 × 7.8 mm, Varian, USA) under the following conditions: mobile phase 0.05 mol $\mathrm{l}^{-1}$ sulfuric acid, flow rate 0.5 ml/min, and column temperature 30 °C. The volume injected was 20 µl.

Characterization experiments of pulps and paper sheets involved the following parameters: pulp yield (Tappi 257), kappa number (Tappi 236), brightness (Tappi 525), viscosity (UNE 57039), tensile index (UNE 57054), burst index (UNE 57058) and tear index (UNE 57-033-86).

### 2.2. Autohydrolysis process

Wood chips and water were mixed in the desired proportions and reacted in a 2 l stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated up to maximum temperatures in the range 160–200 °C with external electric heaters. In Fig. 1 the temperature profile during the heating process of the reactor is shown. The reaction media were heated during the desired time, depending on the required temperature (Fig. 1), and then cooled and samples of the suspensions were withdrawn. The solid/liquid ratio was fixed (1/8) and held constant in all experiments. At the end of treatment, the solid residue was recovered by filtration and washed with distilled water. A fraction was used for pulping and another fraction was air-dried and milled to a particle size <0.5 mm. Milled samples were assayed for cellulose, hemicellulose, lignin and acetyl groups using the same methods as for raw material analysis. An aliquot of liquors was filtered through 0.45 µm membranes and used for direct HPLC determination of monosaccharides, furfural and acetic acid. A second aliquot of liquors (25 ml) was subjected to quantitative posthydrolysis (with 4% sulfuric acid at 121 °C during 60 min) before HPLC analysis. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers and acetyl groups bound to oligosaccharides (Vázquez et al., 2005).

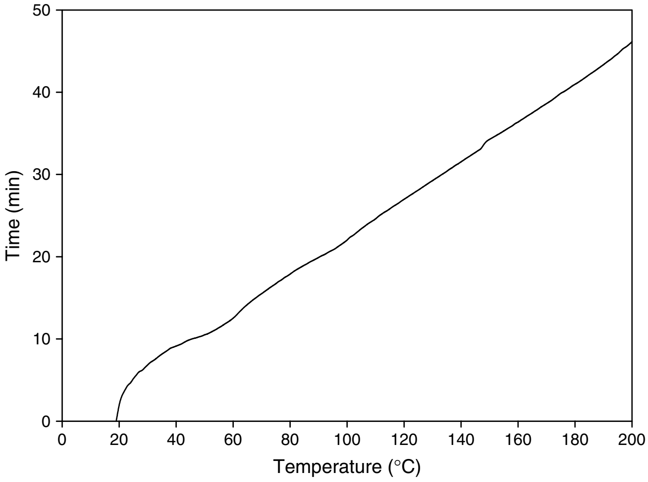

Fig. 1. Temperature profile in reactor during the heating process.

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### 2.3. Pulping process

Pulps were obtained in the same reactor used in the autohydrolysis process. The initial liquor to solid ratio was 8:1 (dry wt. basis), with 10% of soda and 0.5% of anthraquinone (dry wt. basis), the ethanol concentration in the cooking liquor were 20%, 40% and 60% by weight, temperature were 150, 165, and 180 °C and pulping time were 30, 60 and 90 min. The reactor was then closed and simultaneously heated and actuated to assure good mixing and uniform swelling of chips of *Paulownia fortunei*. When it finish the pulping time, the reactor is chilled establishing the temperature of the controller to 25 °C.

Following cooking, the pulp was separated from the liquor and disintegrated, without disturbing the fibers, during 3 min, washed on a sieve of 0.16 mm mesh, defibered and passed through a Strainer filter (0.4 mm mesh) in order to isolate the uncooked material.

### 2.4. Statistical analysis by adaptative neural fuzzy inference system (ANFIS)

ANFIS modelling, proposed by Jang (1993) and based on the first order Sugeno-fuzzy modelling has been successfully applied to the simulation and control of several processes (Smits et al., 1994; Boskovic and Narendra, 1995; Emmanouilides and Petrou, 1997; Roeva and Pencheva, 2005). In that form, the ANFIS paradigm used is a multilayer feed forward back-propagation network. An adaptive network that is functionally equivalent to a Sugeno-fuzzy model has been constructed. The adaptive network can tune the fuzzy system with a back-propagation algorithm based on the collection of input–output data. This provides fuzzy system the ability to learn. The detailed architecture and learning procedure for ANFIS can be found in related literature (Jang and Sun, 1995).

The mathematical equation which responses to different rules is

$$\mathrm{Ye} = \frac{\sum_{j=1}^{m} c_j \left[\prod_{i=1}^{n} x_i\right]}{\sum_{j=1}^{m} \left[\prod_{i=1}^{n} x_i\right]} \tag{1}$$

where Ye is the estimate value of output variable, $m$ the number of rules, $c_i$ a constant term (singleton defuzzifier), $n$ the number of operational variables, $x_i$ the selected membership function.

## 3. Results and discussion

### 3.1. Raw material characteristics

The chemical characterization of *Paulownia fortunei* and other woods are shown in Table 1 (Ebringerová and Heinze, 2000; De Vrije et al., 2002; Garrote et al., 2003; Ververis et al., 2004), where the *Eucalyptus globulus* was used as reference. In this table the comparison with paulownia properties reported by Jiménez et al. (2005), shows certain variations in properties, this indicates that uncontrollable factors such as weather and water availability play a significant role in controlling the measured properties. As can be seen in that Table, paulownia wood yielded lower values in holocellulose and glucan content as regards the paulownia reported by Jiménez et al., *Eucalyptus globulus* and the others alternative raw materials. Klason lignin values are slight higher and xylan, araban and acetyl groups values are similar than that found for the others materials. Then, *Paulownia fortunei* wood could be an adequate raw material for autohydrolysis and pulping processes.

### 3.2. Autohydrolysis process

Several experiences from nonisothermal autohydrolysis were carried out in order to study the effect the severity of the process on the xylooligomer production. Based on previous experiences (Garrote et al., 2003), the operations were carried out at seven different temperatures: 160, 170, 175, 180, 185, 190 and 200 °C.

In Table 2 the variations with the temperature of the different analyzed compounds of the liquid phase are shown. The glucose displays few variations, being its concentration between 0.92 and 0.71 g/l. These values are around 2% of the initial cellulose in the raw material; it suppose that a slight solubilization of this component has been found. Xylose concentrations are higher than the other ones, so their values have increased from 1.05 g/l at 160 °C to 1.89 g/l at 200 °C, although it only means around 4–7% of the initial xylan. Arabinose concentration increases from

Table 1
Chemical composition of *Paulownia fortunei* and other pulp raw materials[a]

| | *Paulownia fortunei* | | *Eucalyptus globulus* (Garrote et al., 2003; Ververis et al., 2004) | | Kenaf (De Vrije et al., 2002) | Miscan-thus (Ververis et al., 2004) | Aspen (Ebringerová and Heinze, 2000) |
|---|---|---|---|---|---|---|---|
| | Present study | Jiménez et al. (2005) | | | | | |
| Holocellulose | 56.9 (1.4)[b] | 71.0 | 66.9 | n.d. | n.d. | n.d. | n.d. |
| Klasson lignin | 27.2 (0.1) | 22.4 | 22.9 | n.d. | 13.4 | n.d. | 19.3 |
| Glucan | 34.2 (0.9) | 37.4 | 46.8 | 53.4 | 40 | 39.5 | 36.3 |
| Xylan | 18.3 (0.2) | n.d. | 16.6 | 14.2 | 19 | 19 | 22.7 |
| Araban | 1.1 (0.1) | n.d. | 0.5 | 0.4 | 1.8 | 1.8 | 0.6 |
| Acetyl groups | 3.3 (0.6) | n.d. | 3.6 | n.d. | n.d. | n.d. | n.d. |

[a] Percentages oven dry matter basis.

[b] Standard deviations are shown within parenthesis.

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Table 2
Variation in the concentration (g/l) of the analyzed compounds among temperatures

| $T_{max}$ (°C) | Glucose | Xylose | Arabinose | Acetic acid | HMF[a] | Furfural | Oligomers |
|---|---|---|---|---|---|---|---|
| 160 | 0.92 | 1.05 | 0.22 | 0.29 | 0.01 | 0.01 | 2.61 |
| 170 | 1.10 | 1.14 | 0.41 | 0.40 | 0.01 | 0.03 | 5.45 |
| 175 | 1.12 | 1.22 | 0.44 | 0.45 | 0.02 | 0.03 | 8.08 |
| 180 | 1.05 | 1.25 | 0.47 | 0.50 | 0.03 | 0.07 | 9.81 |
| 185 | 1.05 | 1.44 | 0.55 | 0.66 | 0.04 | 0.09 | 10.36 |
| 190 | 0.93 | 1.61 | 0.60 | 0.93 | 0.05 | 0.14 | 14.66 |
| 200 | 0.71 | 1.89 | 0.59 | 1.23 | 0.09 | 0.30 | 18.57 |

[a] HMF: 5-hydroxymethylfurfural.

Table 3
Fractionation and composition of solid residue and liquid phase after autohydrolysis process at 190 °C

| | | |
|---|---|---|
| Solid yield (%) | | 78.0 |
| Non volatile solids content (%) | | 19.1 |
| Volatile solids content (%) | | 2.9 |
| Composition of solid residue[a] (%) | Glucan | 41.4 |
| | Xylan | 11.9 |
| | Araban | 0.5 |
| | Acetyl groups | 2.0 |
| | Lignin | 35.9 |
| Composition of liquid phase[b] (%) | Glucose | 0.7 |
| | Xylose | 1.1 |
| | Arabinose | 0.4 |
| | Acetic acid | 0.5 |
| | HMF[c] | 0.0 |
| | Furfural | 0.1 |
| | Gluco-oligomers | 1.3 |
| | Xylo-oligomers | 6.3 |
| | Arabino-oligomers | 0.6 |
| | Acetyl-oligomers | 1.2 |

[a] Percentages oven dry matter basis.
[b] Percentages of extraction with respect to initial raw material.
[c] 5-Hydroxymethylfurfural.

0.22 g/l at 160 °C to 0.59 g/l at 200 °C, which means among 13% and 37% of the initial araban. Acetic acid concentration increases from 0.29 g/l at 160 °C to 1.23 g/l at 200 °C. This increase could be justified by the hydrolysis of acetyl groups which can compose the hemicellulosic fraction linked to xylose monomers (Ebringerová and Heinze, 2000). In addition, a slight increase of furfural has been noted, caused by the acid decomposition of the pentosan such as arabinose and xylose and 5-hydroxymethylfurfural (HMF) too, justified by the acid decomposition of hexosan such as glucose (Garrote et al., 2004). HMF concentrations is lower than 0.1 g/l and furfural concentration increase from 0.01 to 0.3 g/l. These low values indicate a little degradation of monomers.

The majority compounds in liquors are the oligomers, increasing from 2.6 g/l at 160 °C to 18.6 g/l 200 °C. All the other analyzed compounds, have been solubilized from 2.49 to 4.8 g/l. These oligomers could be generated by hydrolysis of the hemicellulosic fraction and its compositions are very different among the diverse raw materials (Vázquez et al., 2005).

The composition of the solid residue and the percentages of solubilization of the liquid phase as regards the initial raw material is shown in Table 3. In that form, the composition of the solid residues shows a significant increase of glucan (from 34.18% (Table 1) to 41.44%) and klason lignin (from 27.22% to 35.9%), justified by the low degrada-

Table 4
Values of operational variables and properties of the pulp and paper sheets obtained in the organosolv pulping process using the proposed experimental design

| Temperature | Time | Ethanol concentration | Yield (%) | Viscosity (ml/g) | Kappa number | Tensile index (N m/g) | Burst index (kPa $m^2$/g) | Tear index (mN $m^2$/g) | Brightness (% ISO) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 37.0 | 278 | 52.7 | 21.4 | 0.90 | 0.92 | 16.5 |
| 1 | 1 | −1 | 32.0 | 456 | 40.5 | 21.9 | 0.98 | 1.06 | 29.5 |
| 1 | −1 | 1 | 37.4 | 396 | 49.3 | 24.0 | 1.10 | 1.09 | 18.9 |
| 1 | −1 | −1 | 38.4 | 703 | 46.9 | 28.9 | 1.22 | 1.23 | 27.4 |
| −1 | 1 | 1 | 43.5 | 547 | 74.1 | 20.1 | 0.78 | 0.86 | 17.4 |
| −1 | −1 | 1 | 46.5 | 255 | 66.6 | 17.0 | 0.60 | 0.85 | 17.3 |
| −1 | 1 | −1 | 43.9 | 393 | 45.4 | 19.7 | 0.73 | 1.02 | 24.7 |
| −1 | −1 | −1 | 47.2 | 378 | 73.1 | 18.2 | 0.66 | 1.05 | 22.9 |
| 1 | 0 | 0 | 35.5 | 479 | 46.0 | 22.5 | 0.96 | 0.98 | 24.8 |
| −1 | 0 | 0 | 44.4 | 470 | 61.0 | 19.6 | 0.71 | 0.99 | 22.2 |
| 0 | 1 | 0 | 41.6 | 509 | 55.1 | 21.6 | 0.82 | 0.97 | 23.8 |
| 0 | −1 | 0 | 46.1 | 475 | 57.2 | 19.4 | 0.76 | 1.05 | 22.6 |
| 0 | 0 | 1 | 44.9 | 456 | 65.1 | 19.2 | 0.78 | 0.91 | 18.45 |
| 0 | 0 | −1 | 42.7 | 580 | 50.0 | 22.0 | 0.87 | 1.02 | 26.9 |
| 0 | 0 | 0 | 43.7 | 523 | 53.8 | 19.9 | 0.74 | 0.98 | 23.9 |

Where non normalized values are: temperature 150 °C for normalized −1, 165 °C for 0 and 180 °C for +1; time 30 min for −1, 60 min for 0 and 90 min for +1; and ethanol concentration: 20% for −1, 40% for 0 and 60% for +1.

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tion found in these compounds caused by the authohydrolysis process. The high lignin content could explains the low pulping yields found (Table 4). The hemicellulosic fraction compounds decrease its composition due to the high extraction which take place in the autohydrolysis process.

Moreover, Table 3 evidences that the oligomers (9.4%), manly composed by xylooligomers (6.3%), have been the most solubilized compounds. However, monomers (glucose, xylose, arabinose and acetyl groups) and degradation products (5-hydroxymethylfurfural and furfural) are only solubilized around 2.7% as regards the initial raw material.

### *3.3. Pulping process*

The obtained solid phase after autohydrolysis process to 190 °C is used for pulping process, since as the maximum glucose and xylose contents of liquid phase have been obtained at this temperature, with minimum paper sheets characteristics loss (<10%).

In Table 4 the normalized values of the operational variables and the values of the properties of obtained pulps and paper sheets according to the proposed experimental factorial design ($2^n$) are shown. The values of the operational variables have been proposed based on the literature and

Table 5
Values of the constants $c_i$ and membership functions in the neural fuzzy model for dependent variables with 8 rules

| Rules | Operational variables | | | $c_i$ | | | |
|---|---|---|---|---|---|---|---|
| | Temperature, (°C) | Time (min) | Ethanol concentration (%) | Kappa number | Burst index (kPa $m^2$/g) | Tear index (kN $m^2$/g) | Brightness (% ISO) |
| 1 | Low (150) | Low (30) | Low (20) | 71.4 | 0.63 | 1.04 | 23.4 |
| 2 | Low (150) | Low (30) | High (60) | 66.1 | 0.56 | 0.85 | 17.9 |
| 3 | Low (150) | High (90) | Low (20) | 44.4 | 0.72 | 1.02 | 25.4 |
| 4 | Low (150) | High (90) | High (60) | 74.3 | 0.77 | 0.87 | 18.1 |
| 5 | High (180) | Low (30) | Low (20) | 45.7 | 1.17 | 1.20 | 28.0 |
| 6 | High (180) | Low (30) | High (60) | 49.2 | 1.04 | 1.07 | 19.5 |
| 7 | High (180) | High (90) | Low (20) | 40.0 | 0.95 | 1.03 | 30.2 |
| 8 | High (180) | High (90) | High (60) | 53.4 | 0.86 | 0.90 | 17.3 |
| $R^2$ | – | – | – | 0.99 | 0.97 | 0.96 | 0.99 |
| Membership functions are defined by | | | | Low | | $x_i = 1 - \frac{1}{x_{\text{high}} - x_{\text{low}}}(x - x_{\text{low}})$ | |
| | | | | High | | $x_i = \frac{1}{x_{\text{high}} - x_{\text{low}}}(x - x_{\text{low}})$ | |

Table 6
Values of the constants $c_i$ and membership functions in the neural fuzzy model for dependent variables with 8 rules with 12 rules (3 levels for temperature)

| Rules | Operational variables | | | $c_i$ | | |
|---|---|---|---|---|---|---|
| | Temperature, (°C) | Time (min) | Ethanol concentration (%) | Yield (%) | Viscosity (ml/g) | Tensile index (N m/g) |
| 1 | Low (150) | Low (30) | Low (20) | 47.2 | 379 | 18.3 |
| 2 | Low (150) | Low (30) | High (60) | 46.3 | 257 | 17.2 |
| 3 | Low (150) | High (90) | Low (20) | 43.9 | 393 | 19.7 |
| 4 | Low (150) | High (90) | High (60) | 43.4 | 569 | 20.3 |
| 5 | Medium (165) | Low (30) | Low (20) | 45.4 | 564 | 20.5 |
| 6 | Medium (165) | Low (30) | High (60) | 47.5 | 425 | 17.4 |
| 7 | Medium (165) | High (90) | Low (20) | 40.5 | 590 | 23.0 |
| 8 | Medium (165) | High (90) | High (60) | 43.1 | 482 | 20.3 |
| 9 | High (180) | Low (30) | Low (20) | 37.7 | 718 | 29.1 |
| 10 | High (180) | Low (30) | High (60) | 36.4 | 397 | 24.1 |
| 11 | High (180) | High (90) | Low (20) | 31.2 | 450 | 21.5 |
| 12 | High (180) | High (90) | High (60) | 36.4 | 266 | 21.2 |
| $R^2$ | – | – | – | 0.99 | 0.99 | 0.99 |
| $L$ | – | – | – | 6.36 | 6.36 | 6.36 |
| Membership function for variables with two levels | | | | Low | $x_i = 1 - \frac{1}{x_{\text{high}} - x_{\text{low}}}(x - x_{\text{low}})$ | |
| | | | | High | $x_i = \frac{1}{x_{\text{high}} - x_{\text{low}}}(x - x_{\text{low}})$ | |
| Membership function for variables with three levels (*L* is the width of the gaussian membership function) | | | | Low | $x_i = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{low}}}{L}\right)^2\right)$ | |
| | | | | Medium | $x_i = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{medium}}}{L}\right)^2\right)$ | |
| | | | | High | $x_i = \exp\left(-0.5 \cdot \left(\frac{x - x_{\text{high}}}{L}\right)^2\right)$ | |

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experience (Jiménez et al., 2001, 2002b; Diaz et al., 2004) in order to maximize knowledge process with a minimum amount of resources (Table 2), and then develop the empirical models. In that form, the normalized and absolutes (in bracket) values fixed for temperature are −1 (150 °C), 0 (165 °C) and 1 (180 °C), for time are −1 (30 min), 0 (60 min) and 1 (90 min) and for ethanol concentration are −1 (20%), 0 (40%) and 1 (60%).

In the Tables 5 and 6 are shown the values of the constant $c_i$ in the Eq. (1), by using the ANFIS tool in the Matlab 6.5 software suite.

According the constant values of the models (Tables 5 and 6), the fact which makes temperature the most influential variable on the characteristics of the pulps be deduced. Nevertheless, a significant influence of all operational variables for every dependent variables that characterize the pulps and paper sheets is observed.

The different models (Tables 5 and 6) were analyzed in order to determine the range of the operational variables giving the optimum values of all dependent variables. Moreover, the response surface for kappa number and viscosity of the pulps and physical properties of paper sheets were plotted at maximum and minimum levels of the most strongly operational variable (Figs. 2–6) in order to determine the range of the operational variables giving the optimum values of those dependent variables.

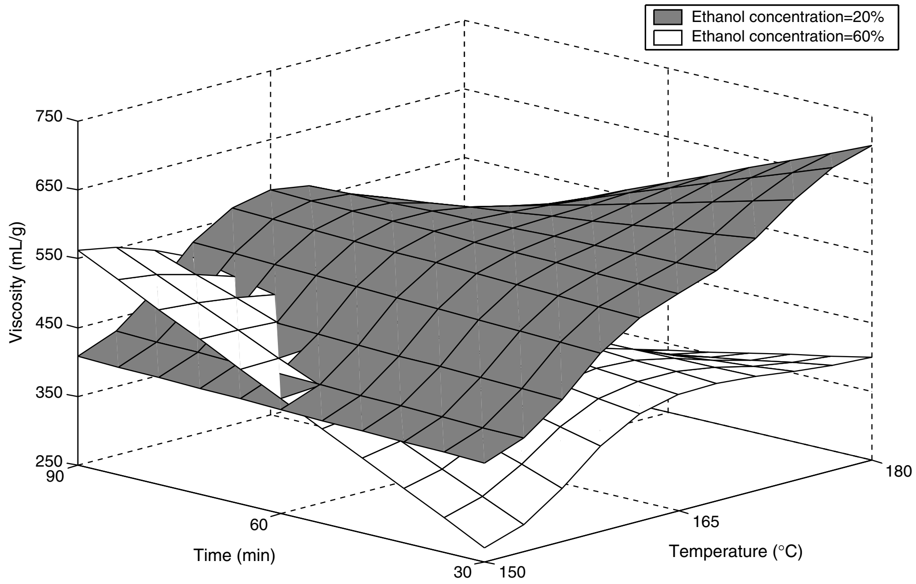

Fig. 2. Variation of viscosity as a function of temperature and time at two ethanol concentration levels.

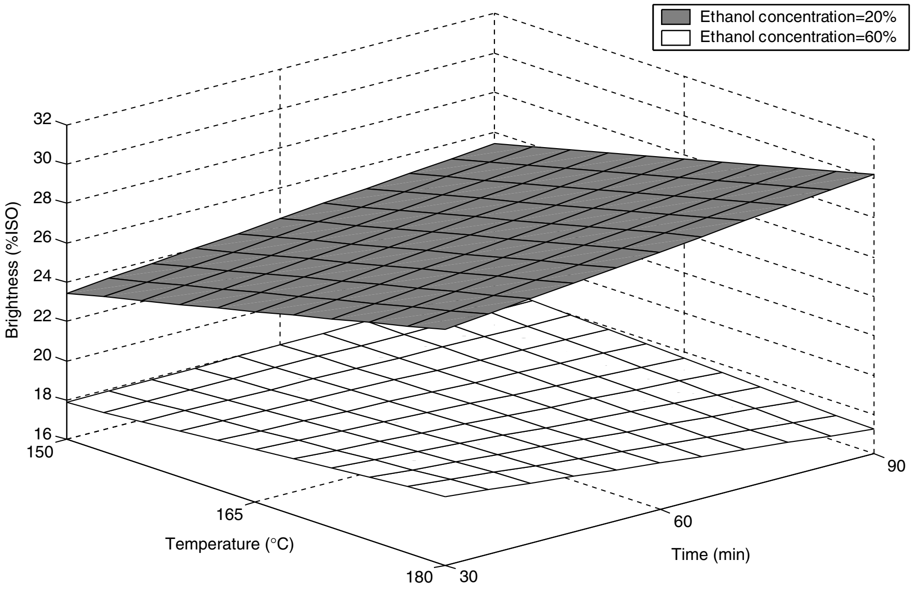

Fig. 3. Variation of brightness as a function of temperature and time at two ethanol concentration.

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According to the constant values showed in the Table 6, temperature displays a high negative influence on the yield, justified by the hydrolysis of residual lignin–hemicellulose bonds (Pereira et al., 1986). Moreover, a low influence of ethanol concentration and a positive influence of pulping time on yield is found. Then, the highest yield (47%) (as regards the initial material to pulping process) is obtained at low values of the pulping temperature, low time and high ethanol concentration.

As can be seen from Table 5, the kappa number was more sensitive to temperature changes than in the others operational variables. Negative influences (higher kappa number) of temperature and time have been found. However, a positive influence for ethanol concentration has been noted. Then, the employment of a low ethanol concentration, high pulping temperature and a long pulping time is advisable in order to produce pulps with a low kappa number.

In Fig. 2, a high negative influence of ethanol concentration on viscosity is observed. In addendum, a low influence of ethanol concentration at low temperatures and high pulping time is noted. The viscosity values are higher at high values of temperature, low ethanol concentration and short pulping time. The influence of ethanol concentration could be justified by inhibition in solvolysis reactions promoted by lower ethanol concentration. Higher ethanol concentra-

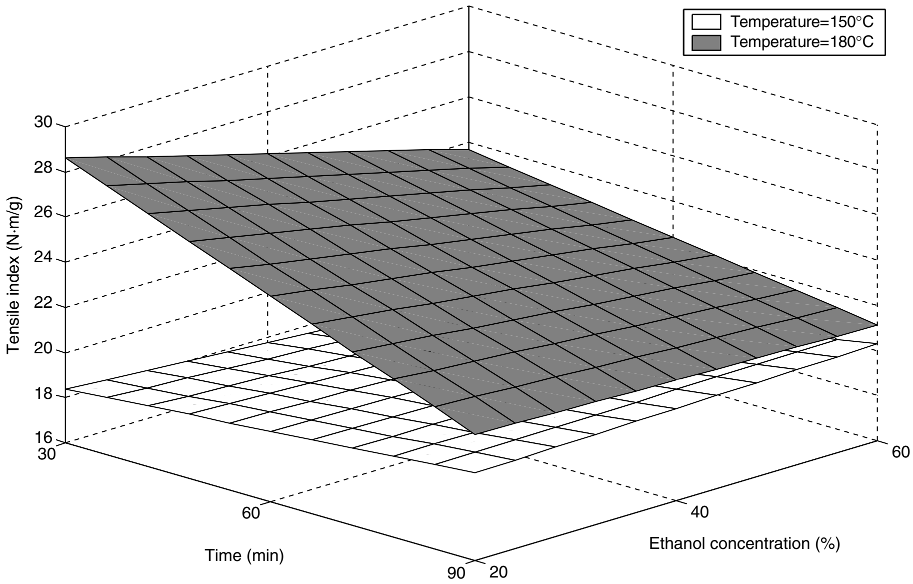

Fig. 4. Variation of tensile index as a function of time and ethanol concentration at two pulping temperature levels.

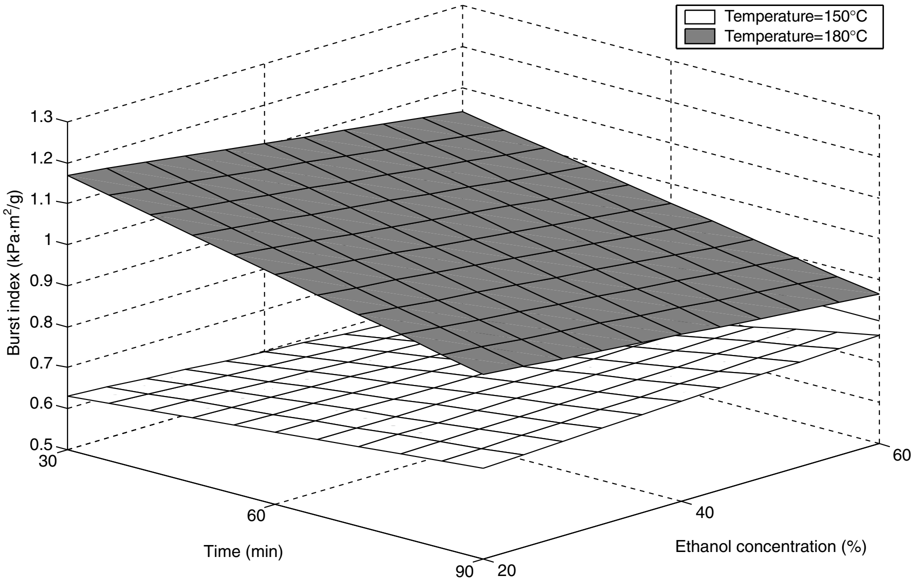

Fig. 5. Variation of burst index as a function of time and ethanol concentration at two pulping temperature levels.

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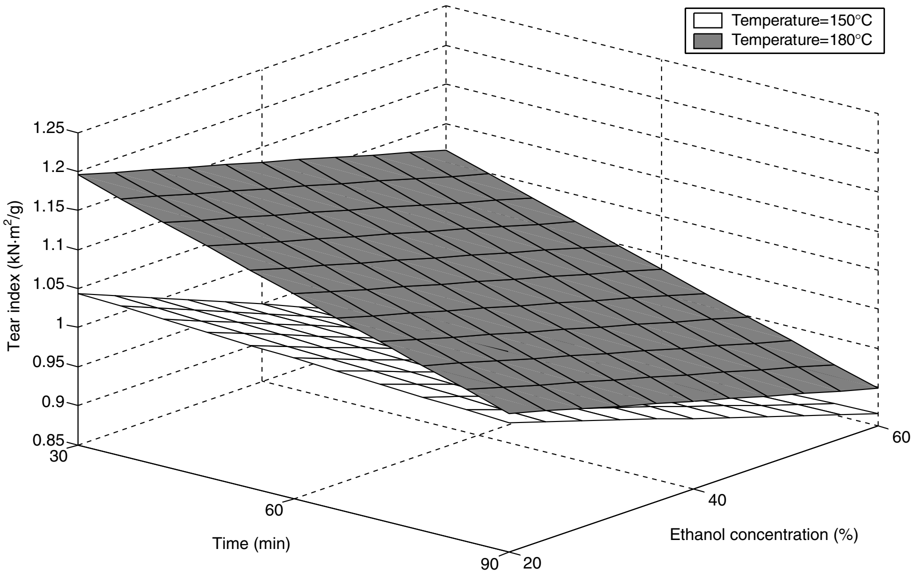

Fig. 6. Variation of tear index as a function of time and ethanol concentration at two pulping temperature levels.

tion could reduce the viscosity of the pulping liquor, which makes possible a better penetration and diffusion of chemicals into wood chips, and therefore, both the average molecular weight of the cellulose obtained and the viscosity values decrease (Oliet et al., 2002).

As can be seen in Fig. 3, the brightness evolution has found to be similar to those observed for kappa number and viscosity. Then, a high negative influence of ethanol concentration is found on brightness values. Moreover, a positive influence of time pulping and temperature is noted. The brightness values are higher at high values of temperature, long pulping time and low ethanol concentration.

Furthermore, a similar evolution is found for tensile index, burst index and tear index (Figs. 4–6), related to the physical properties of the paper sheets. In those figures, a high positive influence for temperature and a negative influence for pulping time have been noted. The ethanol concentration is the lowest influence parameter among the operational variables. Then, operating at high temperatures, short pulping times and low ethanol concentrations is advisable to produce paper sheets with high physical properties.

## 4. Conclusions

The ethanol–water pulping could be a suitable process for solid residues from autohydrolysis process of *P. fortunei* L.

A valuable liquid phase could be obtained from autohydrolysis process. In that phase, a greater increment of oligomers content has been found from 185 to 200 °C. Nevertheless, maximum glucose and xylose contents and minimum paper properties loss, have been obtained at 190 °C.

Pulping temperature has the higher influence on the pulping dependent variables. An increment in pulping temperature has a positive effect on kappa number and viscosity values. However, it has a negative effect on the yield.

Suitable properties of paper sheets and acceptable yield, viscosity and kappa number of the pulps could be obtained by operating at high temperature (180 °C), short pulping time (30 min) and low ethanol concentration (20%). With those conditions, it could be obtained paper sheets with 27.4% ISO brightness, 28.87 N m/g tensile index, 1.22 kPa m$^2$/g burst index and 1.23 kN m$^2$/g tear index.

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# Optimization of *Paulownia Fortunei L.* Autohydrolysis−Organosolv Pulping as a Source of Xylooligomers and Cellulose Pulp

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This paper will consider the influence of the autohydrolysis pretreatment on *Paulownia fortunei L.* woods to obtain a liquid phase (which can be used as a commercial source of organic reagents) and also a solid phase (which is valuable as raw material for pulping processes). Moreover, the influence of the operating conditions—viz., ethanol concentration (20%−60%), temperature (150−180 °C), and pulping time (30−90 min)—on the organosolv pulping (the initial liquor-to-solid ratio was 8:1, with 10% of soda and 0.5% of anthraquinone) of the obtained *Paulownia fortunei L.* solid after the autohydrolysis process has been considered to determine the best pulping conditions and characteristics of the solid phase. In that form, the yield, kappa number, glucan and lignin contents, and tensile index values of the resulting pulps and paper sheets have been studied. The optimum of solubilized components has been obtained at 190 °C (0.92 g/L glucose, 1.61 g/L xylose, 0.60 g/L arabinose, 0.93 g/L acetic acid, 0.047 g/L 5-hydroxymethylfurfural, 0.141 g/L furfural, and 14.66 g/L oligomers). Under these conditions, a suitable chemical composition of pulps and acceptable yield (38%), kappa number (45), and tensile index (28.87 N m/g) could be obtained through operation at high temperature (180 °C), short pulping time (30 min), and low ethanol concentration (20%).

## 1. Introduction

Lignocellulosic materials are one of the most important renewable sources of the terrestrial ecosystem and have been used for many purposes (mainly agricultural-, cattle-, and industrial-type applications). For that reason, new environmentally friendly techniques have been developed to refine these materials, such as autohydrolysis.[1−3] The autohydrolysis process, which is based on the utilization of water as the sole fractionation agent, helps to obtain a rich mixture of oligomers and some monomers, such as glucose, mannose, galactose, arabinose, xylose, etc., that can be used as a commercial source of organic reagents.[1] In addition, the obtained solid fraction from this treatment, which is rich in lignin and cellulose, could be used as raw material for alcohol production,[4] ruminant feed,[5] etc. Particularly, the use of this solid fraction as raw material for pulp and papermaking is an interesting alternative.[6]

On the other hand, the cellulose pulping processes that are based on a sulfur-free organic solvent could be considered as an important alternative to kraft and sulfite processes, because of the use of less-polluting and easily recoverable reagents, such as organic dissolvents.[7] In this way, organosolv pulping circumvents the environmental problems that are related to sulfur emissions, and it has been observed to be effective on several wood species with a broad range of organic solvents.[8] Little waste is produced by the process, and low alcohol contents are recovered easily by distillation; therefore, a relatively low capital investment is required. However, fibers produced by the organosolv process are weaker than those recovered by the kraft process. The papers produced from organosolv pulp then are suitable for uses where strength is not the most important property.[9]

In this sense, a multitude of organic dissolvent has been used, with or without the addition of catalysts (acids, bases, and salts),[10,11] with ethanol being one of the most promising, because of its high power for dissolving lignin and its easy recovery.[12]

Both market demand and environmental pressure have faced the pulp and paper industry, and, to some extent, wood has been replaced by annual plants, fast growth plantations, and agricultural residues.[13,14]

Under this perspective, *Paulownia fortunei L.* (Paulownia) could be considered as an interesting raw material. Paulownia is a plant that originates from China, where it has been well-known for more than 2600 years. It is possible to consider it as a low-water-demand plant, despite not growing in barren zones. In a year of growth, it can develop the equivalent to several years of other species,[15] because of its fast generation of biomass. Paulownia may grow in intensive plantations with ∼2000 trees per hectare. (Hectare is abbreviated as ha.) This is a reason to consider that each tree could produce a cubic meter of wood at the age of 5−7 yrs. An annual production of ∼330 tons/ha then is calculated, although a more conservative number could be 150 tons/ha.[16]

Paulownia has several applications (it has long been used in the manufacture of moldings, cabinets, veneers, furniture, and musical instruments);[17,18] one of the applications is its use to obtain cellulose pulp.[19] The most suitable variety of Paulownia for this purpose is the *Paulownia fortunei L.*, which has an average fiber length of 1.42 mm.[19] This variety is characterized by its fast development and a uniform and regular growth.[17]

This plant could be susceptible to produce xylooligomers under a hydrolytic process, as well as provide a low degraded lignocellulosic residue to the pulping process, which is justified by some Paulownia characteristics, such as its growth and physicochemical properties. This paper examines the influence

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of temperature of the autohydrolysis treatment on the xylooligomers extraction, as well as the suitability of the resulting solid phase for a subsequent pulping; the influence of selected operational variables (viz., ethanol concentration, temperature, and pulping time) on the yield, kappa number, tensile index, and chemical composition of the resulting pulps is analyzed.

## 2. Experimental Section

**2.1. Characterization of the Raw Material and Pulp.** Paulownia wood trimming samples were milled to pass an 8-mm screen, because no diffusional limitations were observed for this particle size in preliminary studies. Samples were air-dried, homogenized in a single lot (to avoid differences in composition among aliquots), and stored. Three aliquots from the homogenized wood lots were subjected to moisture determination (drying at 105 °C to constant weight), quantitative acid hydrolysis with 5 mL of 72% $H_2SO_4$ for one hour, and quantitative post-hydrolysis with 4% $H_2SO_4$ (adding water until 148.67 g) at 121 °C for 60 min. Before high-performance liquid chromatography (HPLC) analysis, the solid residue from the post-hydrolysis stage was recovered by filtration and considered to be Klason lignin.

The monosaccharides and acetic acid contained in hydrolysates were determined using HPLC, to estimate (after corrections for stoichiometry and sugar decomposition) the contents of samples in α-cellulose (as glucan), hemicelluloses (xylan, araban, and acetyl groups), and holocellulose, which would be calculated by adding the amounts of glucan, xylan, araban, acetyl groups and uronic acids. The moisture in the wood was considered as water in the material balances. In that form, α-cellulose is glucan and holocellulose is adding glucan, xylan, araban, and acetyl groups. Chromatographic separation was performed using an ion-exchange resin Metacarb 87H column (300 mm × 7.8 mm, Varian, Palo Alto, CA) under the following conditions: mobile phase, 0.05 mol/L of sulfuric acid; flow rate, 0.5 mL/min; and column temperature, 30 °C. The volume injected was 20 $\mu$L.

Characterization experiments of pulps and paper sheets involved the following parameters: pulp yield (Tappi 257), kappa number (Tappi 236), and tensile index (UNE 57054). Pulp samples were assayed for cellulose (as glucan), xylan, lignin, and acetyl groups, using the same methods as those used for raw wood analysis.

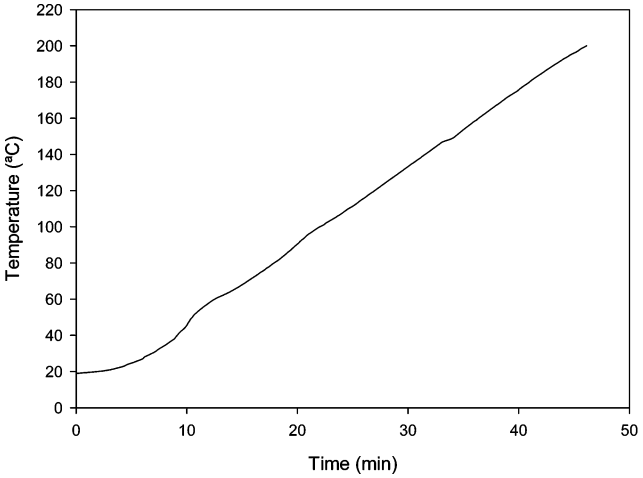

**Figure 1.** Temperature profile in reactor during the heating process.

**Table 1. Simplification of eq 1 for the Dependent Variables Analyzed**

| number of fuzzy rules | eq 1 simplified to[a] |
|---|---|
| 8[b] | $y_e = \dfrac{\sum_{l=1}^{8} c_l[\prod_{i=1}^{3} x_i]}{\sum_{l=1}^{8} [\prod_{i=1}^{3} x_i]}$ |
| 12[c] | $y_e = \dfrac{\sum_{l=1}^{12} c_l[\prod_{i=1}^{3} x_i]}{\sum_{l=1}^{12} [\prod_{i=1}^{3} x_i]}$ |

[a] $c_i$ is a constant term (Singleton defuzzifier). [b] Two levels for all independent variables. [c] Three levels for one independent variable and two levels for the other variables.

**2.2. Autohydrolysis Pretreatment Procedure.** Wood chips and water were mixed in the desired proportions and reacted in a 2-L stainless steel Parr reactor that was fitted with double four-blade turbine impellers. The vessels were heated from 160 °C to 200 °C (in steps of 160, 170, 175, 180, 185, 190, and 200 °C) with external electric heaters. The temperature profile during the heating process of the reactor is shown in Figure 1. The reaction medium was heated during the desired time, depending on the required temperature (see Figure 1), and then cooled. After achieving normal pressure (monitored by manometer implemented in the reactor), the reactor was opened and samples of the suspensions were withdrawn. The solid-to-liquid ratio was fixed (1:8) and held constant in all experiments. This value is the minimum value that allows a homogeneous mixture. At the end of treatment, the solid residue was recovered by filtration and washed with distilled water. A fraction was used for pulping and another fraction was air-dried and milled to a particle size of <0.5 mm. Milled samples were assayed for cellulose, hemicelluloses, lignin, and acetyl groups, using the same methods as those used for raw material analysis. Moreover, the volatile compounds content was measured in the autohydrolysis liquor until a constant weight was obtained, using an oven (105 °C). This weight was referenced as the initial raw material contend. The volatile compound content was determined by the relation

$$\text{volatile content} = 100 - \text{solid yield} - \text{nonvolatile content}$$

An aliquot of liquors was filtered through 0.45 $\mu$m membranes and used for direct HPLC determination of monosaccharides, furfural, and acetic acid. A second aliquot of liquors (25 mL) was subjected to quantitative post-hydrolysis (with 4% $H_2SO_4$ at 121 °C for 60 min) before HPLC analysis. The increase in the concentrations of monosaccharides and acetic acid caused by post-hydrolysis provided a measure of the concentrations of oligomers[1] and acetyl groups that were bound to oligosaccharides.

**2.3. Pulping Procedure and Formation of Paper Sheets.** Cellulose pulps were obtained in the same reactor that was used in the autohydrolysis pretreatment. The initial liquor-to-solid ratio was 8:1 (oven-dry (od) basis), with 10% of soda and 0.5% of anthraquinone (od basis), and the ethanol concentration in the cooking liquor ranged from 20% to 40% to 60% (by weight); the temperature ranged from 150 °C to 165 °C to 180 °C, and pulping time ranged from 30 min to 60 min to 90 min. The reactor was then closed and simultaneously heated, and the turbine impellers were connected to ensure well mixing and

**Table 2. Chemical Composition of *Paulownia Fortunei* and Other Pulp Raw Materials**[a]

| | *Paulownia fortunei* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Raw Material | | *Eucalyptus globulus* | | | | |
| | present study[b] | present study[c] | ref 29 | ref 30 | ref 6 | ref 31 | Kenaf (ref 32) | *Arundo donax* (ref 33) | Aspen (ref 34) |
| holocellulose | 56.93 (1.38)[d] | 55.77 (1.22) | 78.8 | 70.96 | 66.9 | nd[e] | nd[e] | 64.5 | nd[e] |
| Klason lignin | 27.22 (0.08) | 35.90 (0.05) | 22.1 | 22.4 | 22.9 | nd[e] | 13.4 | 23 | 19.3 |
| glucan | 34.18 (0.88) | 41.44 (0.66) | 48.3 | 37.44 | 46.8 | 53.4 | 40 | 34.8 | 36.3 |
| xylan | 18.31 (0.22) | 11.88 (0.34) | nd[e] | nd[e] | 16.6 | 14.2 | 19 | 19.4 | 22.7 |
| araban | 1.13 (0.08) | 0.45 (0.04) | nd[e] | nd[e] | 0.54 | 0.4 | 1.8 | 1.5 | 0.6 |
| acetyl groups | 3.31 (0.6) | 2.00 (3.1) | nd[e] | nd[e] | 3.56 | nd[e] | nd[e] | 3.4 | nd[e] |

[a] Percentages given on an oven dry matter basis. [b] Raw material. [c] Solid phase after autohydrolysis treatment. [d] Standard deviations are shown within parentheses. [e] Not detected.

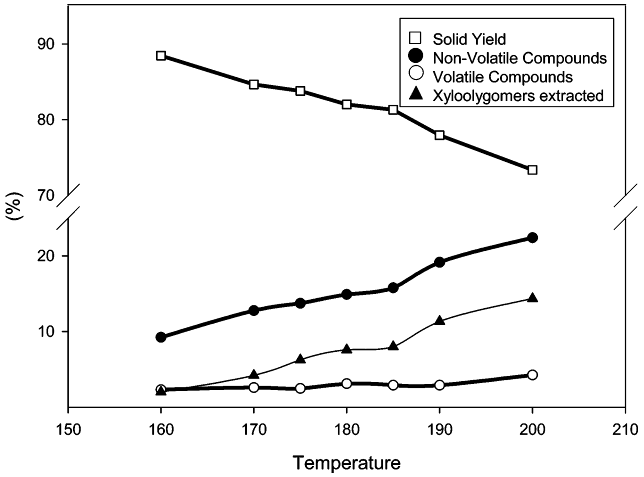

**Figure 2.** Extraction of the different analyzed compounds (given as a percentage, with respect to initial raw material) in the autohydrolysis liquor.

**Table 3. Variation in the Concentration of the Analyzed Compounds among Temperatures**

| | Concentration (g/L) | | | | | | |
|---|---|---|---|---|---|---|---|
| temperature, *T* (°C) | glucose | xylose | arabinose | acetic acid | HMF[a] | furfural | oligomers |
| 160 | 0.92 | 1.05 | 0.21 | 0.29 | 0.01 | 0.01 | 2.60 |
| 180 | 1.05 | 1.24 | 0.47 | 0.50 | 0.02 | 0.07 | 9.81 |
| 190 | 0.93 | 1.61 | 0.60 | 0.93 | 0.05 | 0.14 | 14.66 |
| 200 | 0.70 | 1.89 | 0.59 | 1.23 | 0.09 | 0.30 | 18.56 |

[a] HMF = 5-hydroxymethylfurfural.

uniform swelling of the Paulownia chips. When the pulping time was completed, the reactor was cooled, establishing the temperature of the controller to 25 °C.

Following cooking, the pulp was separated from the liquor and disintegrated, without disturbing the fibers, for 3 min, washed on a sieve of 0.16 mm mesh, defibered, and passed through a Strainer filter (0.4 mm mesh), to isolate the uncooked material.

Paper sheets were prepared with an ENJO-F-39.71 sheet machine, according to the UNE 57042-74 standard.

**2.4. Statistical Analysis by the Adaptative Neural Fuzzy Inference System (ANFIS).** Fuzzy modeling, based on the pioneering idea of Zadeh,[20] is a powerful tool to describe the behavior of nonlinear complex systems. Since the 1980s, fuzzy theory has been successfully applied to the simulation and control of several processes.[21−23]

Another powerful tool for modeling these complex systems is a neural network (NN), which was developed from the analogies to the properties of biological neurons. The most important feature of neural network is their ability to achieve an accurate nonlinear mapping from input−output pairs of data without knowing their functional relationship.[24] NNs have been successfully applied to many areas of assessing biochemical systems.[24,25]

The integration of fuzzy systems and a neural network can combine the merits of both systems and offer a more powerful tool for modeling. A neural fuzzy system is used in applications such as integrated system modeling, which uses NNs as a tool in fuzzy systems.

In that form, an adaptive network-based fuzzy inference system (ANFIS), which was proposed by Jang,[26] is based on the first-order Sugeno fuzzy model. The NN paradigm used is a multilayer feed forward back-propagation network. An adaptive network that is functionally equivalent to a Sugeno fuzzy model has been constructed. The adaptive network can tune the fuzzy system with a back-propagation algorithm that is based on the collection of input−output data. This provides the fuzzy system the ability to learn. The detailed architecture and learning procedure for ANFIS can be found in related literature.[27,28]

The mathematical equation, which responds to different rules, is

$$y_{\mathrm{e}} = \frac{\sum_{l=1}^{m} y_l R_l}{\sum_{l=1}^{m} R_l} \qquad (1)$$

where $y_{\mathrm{e}}$ is the estimated value of the output variable, $m$ the number of rules, $y_l$ the defuzzifier, and $R_l$ the product of the selected membership functions.

The simplification of eq 1 for the variables studied is showed in Table 1. The parameters and constants in the previous equation were estimated using the ANFIS tool in the Matlab software suite (Fuzzy Logic Toolbox Version 2.2.2 and Neural Network Toolbox Version 4.0.6).

## 3. Results and Discussion

**3.1. Raw Material Characteristics.** The chemical characterization of Paulownia raw material and other woods are shown in Table 2 ;[6,29−34] therefore, *Eucalyptus globulus* was used as a reference. In this table, the comparison with Paulownia properties that were reported by Jiménez et al. shows certain variations in properties. This observation lets us know that uncontrollable factors such as weather and water availability have a significant role in controlling the measured properties. In addition, the methodology applied by Jiménez et al.[30] (cellulose by Tappi 203, holocellulose by Wise et al., lignin by Tappi 222 and hemicelluloses by Tappi 203) is different than the methodology used in this paper, which could justify these differences. As can be seen, Paulownia wood yielded lower values in holocel-

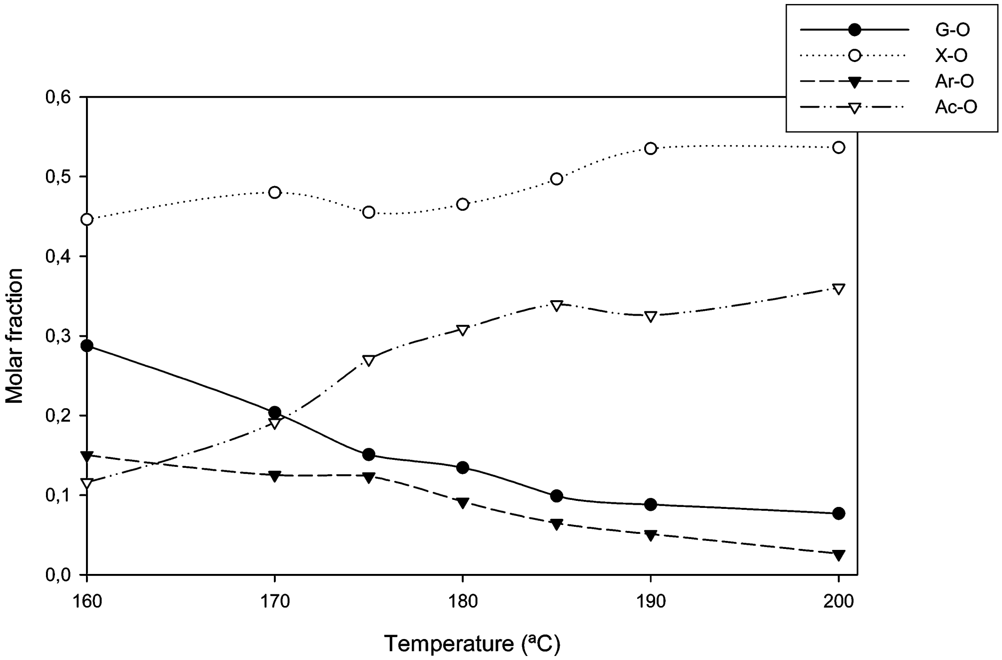

**Figure 3.** Olygomers concentration (G−O, molar fraction of glucose monomers; X−O, molar fraction of xylose monomers; Ar−O, molar fraction of arabinose monomers; and Ac−O, molar fraction of acetic acid monomers).

**Table 4. Values of Independent Variables and Properties of the Pulp Obtained in the Organosolv Pulping Process, Using the Proposed Experimental Design**

| temperature, $T^a$ | time, $t^b$ | ethanol concentration, $EC^c$ | yield (%) | tensile index (N m/g) | kappa number | Concentration (%)<br>glucan | xylan | acetyl groups | lignin |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 37.02 | 21.39 | 52.7 | 72.76 | 7.24 | 1.45 | 13.07 |
| 1 | 1 | −1 | 32.02 | 21.91 | 40.5 | 81.57 | 8.55 | 1.29 | 6.33 |
| 1 | −1 | 1 | 37.35 | 24.02 | 49.3 | 78.71 | 8.46 | 1.52 | 9.72 |
| 1 | −1 | −1 | 38.43 | 28.87 | 46.9 | 81.40 | 7.88 | 1.45 | 6.82 |
| −1 | 1 | 1 | 43.49 | 20.05 | 74.1 | 71.92 | 3.77 | 2.21 | 15.34 |
| −1 | −1 | 1 | 46.53 | 16.97 | 66.6 | 71.21 | 6.66 | 1.26 | 8.10 |
| −1 | 1 | −1 | 43.87 | 19.74 | 45.4 | 73.50 | 7.77 | 1.15 | 3.74 |
| −1 | −1 | −1 | 47.24 | 18.20 | 73.1 | 71.98 | 6.90 | 1.24 | 11.76 |
| 1 | 0 | 0 | 35.51 | 22.46 | 46.0 | 78.70 | 8.50 | 0.70 | 8.30 |
| −1 | 0 | 0 | 44.42 | 19.60 | 61.0 | 73.00 | 7.20 | 0.77 | 11.05 |
| 0 | 1 | 0 | 41.60 | 21.56 | 55.1 | 75.82 | 9.82 | 1.02 | 10.40 |
| 0 | −1 | 0 | 46.10 | 19.43 | 57.2 | 78.29 | 9.70 | 1.04 | 10.88 |
| 0 | 0 | 1 | 44.88 | 19.16 | 65.1 | 77.28 | 9.04 | 1.16 | 9.69 |
| 0 | 0 | −1 | 42.74 | 22.01 | 50.0 | 81.29 | 9.43 | 0.99 | 7.11 |
| 0 | 0 | 0 | 43.73 | 19.94 | 53.8 | 78.32 | 9.07 | 0.95 | 8.24 |

[a] Non-normalized values of temperature are as follows: −1 = 150 °C, 0 = 165 °C, and 1 = 180 °C. [b] Non-normalized values of time are as follows: −1 = 30 min, 0 = 60 min, and 1 = 90 min. [c] Non-normalized values of ethanol concentration are as follows: −1 = 20%, 0 = 40%, and 1 = 60%.

lulose and glucan content, in regard to the Paulownia reported by Jiménez et al.,[30] *Eucalyptus globulus*, and the other alternative raw materials. Klason lignin gives slight higher values, and xylan, araban, and acetyl groups exhibit values similar to those observed for the other materials. Paulownia wood then could be a suitable raw material for autohydrolysis treatment and subsequent pulp and papermaking processes.

**3.2. Autohydrolysis Procedure.** Several experiments from nonisothermal autohydrolysis were conducted to study the effect of the severity of the treatment on the oligomer production. Based on previous experiments,[6] the operations were performed at seven different temperatures (over a range of 160−200 °C). Figure 2 shows a weak influence of the treatment on oligomer extractions (2%) at 160 °C and a strong influence (14.4%) at 200 °C. The use of higher temperature values would imply a decrease in the quality of the obtained cellulose pulps in the subsequent pulping stage. The optimum autohydrolysis conditions then could be used to ensure suitable oligomer extractions and an adequate quality of the cellulose pulp could be obtained.

Moreover, the variation of solid yield and volatile and nonvolatile compound contents in the autohydrolysis liquors is shown in Figure 2. The solid yielded decreases from 88.4 kg of solid material residue/100 kg raw (on dry basis) at 160 °C to 73.4 kg/100 kg at 200 °C. This decrease could be caused by the solubilization of the extractable compounds as well as the hemicellulosic fraction. At these temperatures, cellulose and lignin fractions could remain in the solid phase,[35] so these two fractions attain a value of ∼61.4% of the raw material (by weight). The content in volatile compounds increases from 2.3 kg/100 kg at 160 °C to 4.3 kg/100 kg at 200 °C. These values could be considered low, in comparison to values that can be obtained in more-severe operation conditions. The content of nonvolatile compounds increases from 9.24 kg/100 kg at 160 °C to 20.40 kg/100 kg at 200 °C, because of their solubilization in the liquid phase.

In Table 3, the variation of the different compounds presented in the liquid phase is shown, relative to the temperature. The glucose displays few variations, with its concentration being

**Table 5. Values of the Constants $c_i$ in the Neural Fuzzy Model for Dependent Variables with Eight Rules**

| | Operational Variables | | | Dependent Variables | |
|---|---|---|---|---|---|
| rule | temperature, $T$ | time, $t$ | ethanol concentration | kappa number | lignin concentration (%) |
| 1 | low (150 °C) | low (30 min) | low (20%) | 71.36 | 12.23 |
| 2 | low (150 °C) | low (30 min) | high (60%) | 66.06 | 8.21 |
| 3 | low (150 °C) | high (90 min) | low (20%) | 44.36 | 4.01 |
| 4 | low (150 °C) | high (90 min) | high (60%) | 74.26 | 15.25 |
| 5 | high (180 °C) | low (30 min) | low (20%) | 45.69 | 6.89 |
| 6 | high (180 °C) | low (30 min) | high (60%) | 49.19 | 9.43 |
| 7 | high (180 °C) | high (90 min) | low (20%) | 39.98 | 6.20 |
| 8 | high (180 °C) | high (90 min) | high (60%) | 53.40 | 12.58 |
| $R^2$ | | | | 0.99 | 0.96 |

membership functions are defined by:

low
$$x_i = 1 - \left(\frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}\right)(x - x_{\mathrm{low}})$$

high
$$x_i = \left(\frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}\right)(x - x_{\mathrm{low}})$$

**Table 6. Values of the Constants $c_i$ in the Neural Fuzzy Model for Dependent Variables with 12 Rules (Three Levels for Temperature)**

| | Operational Variables | | | Dependent Variables | | | |
|---|---|---|---|---|---|---|---|
| rule | temperature | time | ethanol concentration | yield (%) | tensile index (N m/g) | glucan concentration (%) | xylan concentration (%) |
| 1 | low (150 °C) | low (30 min) | low (20%) | 47.20 | 18.26 | 71.40 | 6.91 |
| 2 | low (150 °C) | low (30 min) | high (60%) | 46.30 | 17.17 | 70.81 | 6.66 |
| 3 | low (150 °C) | high (90 min) | low (20%) | 43.94 | 19.70 | 73.16 | 7.81 |
| 4 | low (150 °C) | high (90 min) | high (60%) | 43.35 | 20.29 | 71.76 | 3.58 |
| 5 | medium (165 °C) | low (30 min) | low (20%) | 45.38 | 20.53 | 81.68 | 9.61 |
| 6 | medium (165 °C) | low (30 min) | high (60%) | 47.48 | 17.38 | 77.83 | 9.52 |
| 7 | medium (165 °C) | high (90 min) | low (20%) | 40.50 | 23.03 | 79.22 | 10.02 |
| 8 | medium (165 °C) | high (90 min) | high (60%) | 43.07 | 20.26 | 74.91 | 9.55 |
| 9 | high (180 °C) | low (30 min) | low (20%) | 37.74 | 29.08 | 81.24 | 7.85 |
| 10 | high (180 °C) | low (30 min) | high (60%) | 36.40 | 24.07 | 78.62 | 8.47 |
| 11 | high (180 °C) | high (90 min) | low (20%) | 31.20 | 21.52 | 81.57 | 8.54 |
| 12 | high (180 °C) | high (90 min) | high (60%) | 36.41 | 21.16 | 72.48 | 7.18 |
| $R^2$ | | | | 0.99 | 0.99 | 0.98 | 0.99 |
| $L$ | | | | 6.36 | 6.36 | 6.36 | 6.36 |

membership function for variables with two levels

low
$$x_i = 1 - \left(\frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}\right)(x - x_{\mathrm{low}})$$

high
$$x_i = \left(\frac{1}{x_{\mathrm{high}} - x_{\mathrm{low}}}\right)(x - x_{\mathrm{low}})$$

membership function for variables with three levels ($L$ is the width of the Gaussian membership function)

low
$$x_i = \exp\left[-0.5\left(\frac{x - x_{\mathrm{low}}}{L}\right)^2\right]$$

medium
$$x_i = \exp\left[-0.5\left(\frac{x - x_{\mathrm{medium}}}{L}\right)^2\right]$$

high
$$x_i = \exp\left[-0.5\left(\frac{x - x_{\mathrm{high}}}{L}\right)^2\right]$$

between 1.05 g/L and 0.70 g/L. Theses values mean that ∼2% of the initial cellulose is present in the raw material, which implies slight solubilization of this component. The arabinose concentration increases from 0.21 g/L at 160 °C to 0.59 g/L at 200 °C, that is, between 13% and 37% of the initial araban present in the raw material. The xylose concentrations are higher than those of other compounds, so their values increase from 1.05 g/L at 160 °C to 1.89 g/L at 200 °C, although it only means around 4%−7% of the initial xylan. The acetic acid concentration increases from 0.29 g/L at 160 °C to 1.23 g/L at 200 °C. This increment may be produced by the hydrolysis of acetyl groups, which can be found in the hemicellulosic fraction and is linked to xylose monomers.[36] In addition, a slight increase of furfural (justified by the acid decomposition of the pentosan, such as arabinose and xylose) and 5-hydroxymethylfurfural (HMF) (justified by the acid decomposition of hexosan such as glucose)[37] has been noted. The HMF concentration is <0.10 g/L, and the furfural concentration increases from 0.10 g/L to 0.30 g/L. These low values provide evidence that little degradation of the monomers has occurred.

The majority compounds in liquors are the oligomers (see Table 3), increasing from 2.6 g/L at 160 °C to 18.6 g/L at 200 °C. All the other analyzed compounds have been extracted from 2.49 g/L to 4.8 g/L. Oligomers are generated via the hydrolysis of the hemicellulosic fraction and their compositions are very different among the diverse raw materials. However, the majority compounds of hemicelluloses in agricultural raw materials are xylose monomers and acetyl groups.[1]

The composition of these oligomers (in molar fraction) is shown in Figure 3. In this figure, the glucose fraction decreases from 0.29 at 160 °C to 0.08 at 200 °C, and the arabinose fraction decreases from 0.15 at 160 °C to 0.03 at 200 °C. The molar fraction of acetyl groups increases from 0.12 at 160 °C to 0.36 at 200 °C, and the xylose fraction increases slightly from 0.45 at 160 °C to 0.54 at 200 °C. The glucose presence could be justified by minor hydrolysis of glucan (whose extraction was

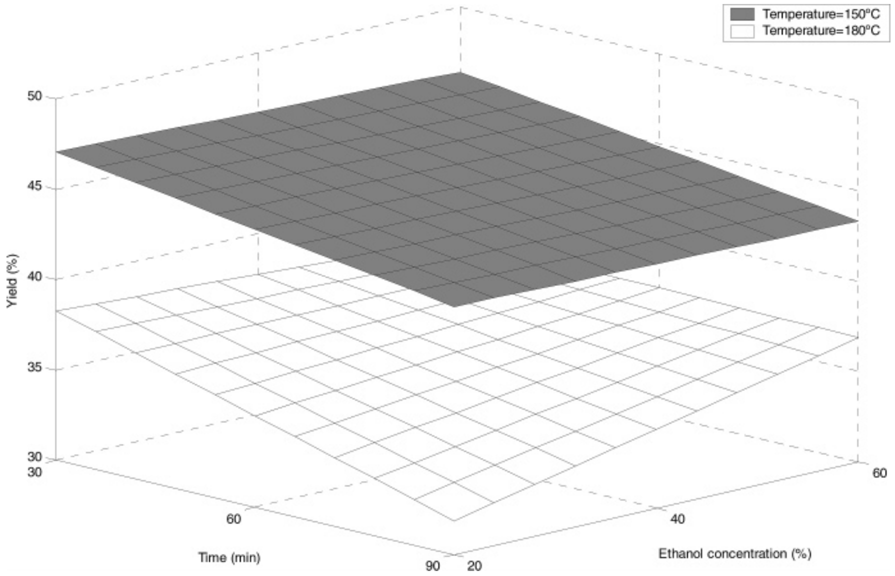

**Figure 4.** Variation of yield as a function of time and ethanol concentration at two pulping temperature levels.

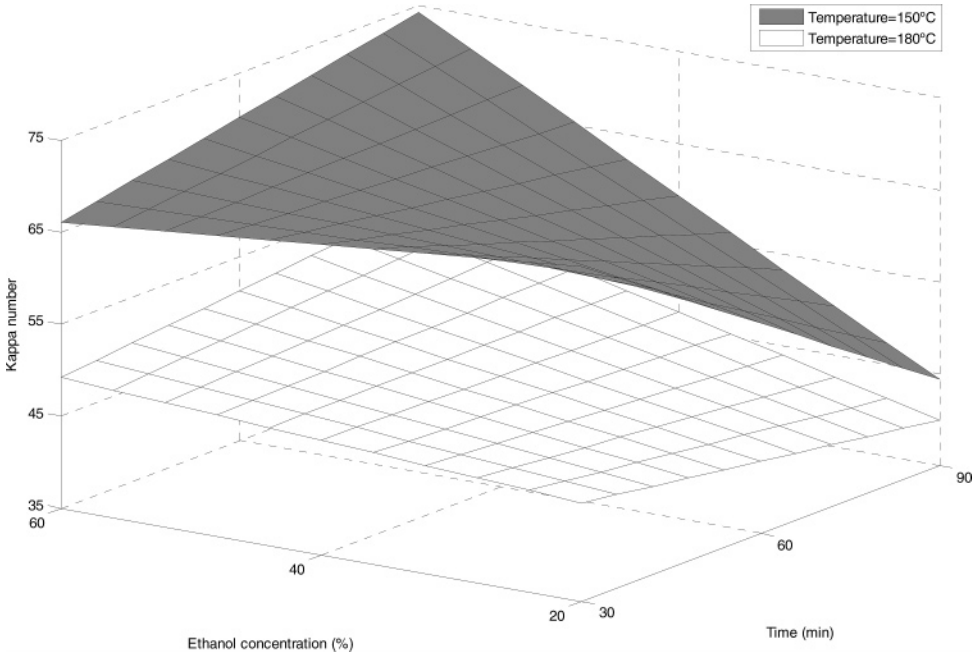

**Figure 5.** Variation of kappa number as a function of time and ethanol concentration at two pulping temperature levels.

∼2−4%, relative to the initial cellulose) or by the presence of glucose heteropolymers in the hemicellulosic fraction.[38] The decrease of its molar fraction could be caused by the increase of the other monomers. The arabinose fraction also decreases. This compound, which usually appears in furanose form, characterized by its high reactivity.[39] Both the xylose and acetyl groups fractions also increase.

**3.3. Properties of the Pulp Obtained. Optimization Studies.** An autohydrolysis temperature of 190 °C was selected as the optimum operation temperature, because it provides high extraction of xylooligomers (11.3%, with regard to the initial raw material), as well as ensuring minimum cellulosic fiber degradation. The solid obtained after the autohydrolysis treatment is used for the pulping process. In Table 2, a comparative analysis among the raw materials (in regard to the solid fraction after autohydrolysis treatment at 190 °C) and other alternative raw materials has been performed. In that form, both the cellulose content and lignin have increased. This observation could be due to the low solubilization of these compounds under the autohydrolysis treatment, and, therefore, their concentrations have increased in the solid phase. In addition, the hemicellulosic fraction contents (xylan, araban, and acetyl groups) have decreased. This effect could be caused by a significative degradation of this fraction.

On the other hand, the normalized values of the independent variables and the properties of obtained cellulose pulps according to the proposed experimental design are presented in Table 4. Based on the literature[6,40,41] and experiments, the values of the applied independent variables of the proposed factorial design (Table 4) have been estimated to maximize the knowledge process with a minimum number of resources. In that form, the values that are fixed for temperature are −1 (150 °C), 0 (165 °C), and 1 (180 °C); those values for time are −1 (30 min), 0 (60 min), and 1 (90 min), and those values for ethanol concentrations are −1 (20%), 0 (40%), and 1 (60%).

According to the constant values of the models (see Tables 5 and 6), it could be deduced that temperature is the most influential variable on the characteristics of the cellulose pulps.

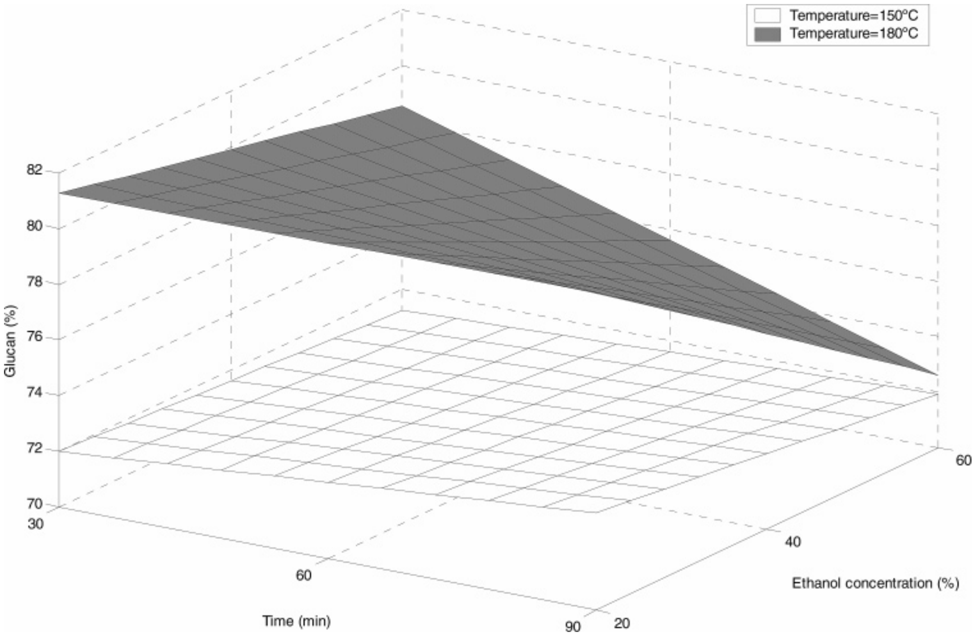

**Figure 6.** Variation of glucan content as a function of time and ethanol concentration at two pulping temperature levels.

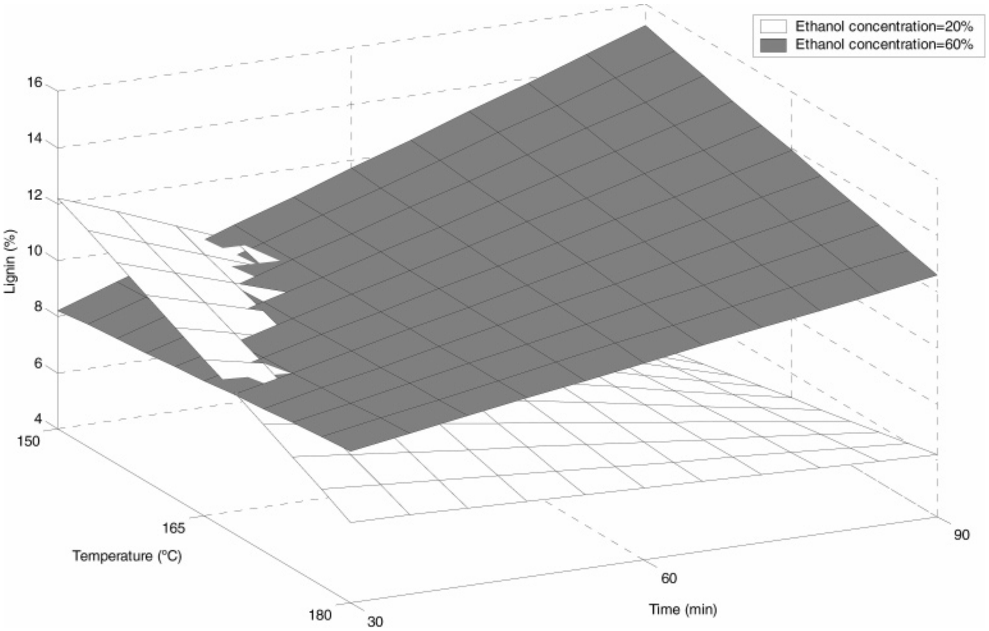

**Figure 7.** Variation of lignin content as a function of temperature and time at two ethanol concentration levels.

Nevertheless, significative terms of the influence of the independent operation variables are observed for all the dependent variables that characterize the cellulose pulps.

The response surfaces for each dependent variable were plotted at the maxima and minima levels of the most strongly independent variable (see Figures 4−8) to determine the values of the independent variables, giving the optimum yield, kappa number, glucan and lignin contents, and tensile index values.

A high negative influence of the temperature on the yield (Figure 4) has been observed, as a consequence of the hydrolysis of residual lignin−hemicellulose bonds.[42] Moreover, the yield was less influenced by the ethanol concentration than by the pulping time, and a positive influence has been observed for ethanol concentration. The highest yield (46%) (relative to the initial material of the pulping process) then is obtained at low temperature, short time, and high ethanol concentration.

As can be seen from Figure 5, the kappa number was more sensitive to temperature changes than the other independent variables. A negative influence (better kappa number) of temperature and time has been observed. However, a positive influence for ethanol concentration has been noted. Therefore, the application of a low ethanol concentration, high pulping temperature, and long pulping time is advisable to produce pulps with a low kappa number.

A very important observation regarding the influence of pulping temperature and glucan content is shown in Figure 6 at low ethanol concentrations. A high influence of ethanol concentration is noted at high temperature. At low temperature, low values of glucan and a slight influence of ethanol concentration and pulping time have been observed. The production of a relatively high glucan pulp is favored by low ethanol concentration, high pulping time, and high temperature.

The lignin content (Figure 7) was more sensitive to changes in ethanol concentration than the other independent variables of the pulping process. The pulping time has a low influence under low values of ethanol concentration. The lowest values

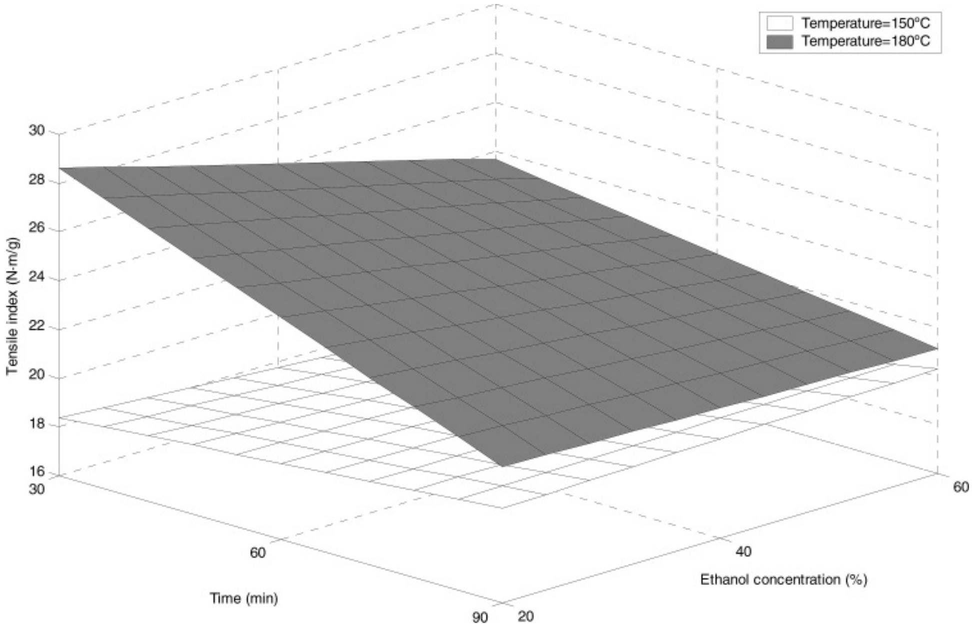

**Figure 8.** Variation of tensile index values as a function of time and ethanol concentration at two pulping temperature levels.

are found at high temperature, long pulping time, and low ethanol concentration. However, both long times and high ethanol concentrations should not be applied jointly, justified by the slight effect of pulping time under those conditions.

According to Figure 8, tensile index is characterized by a high positive influence of temperature and a negative influence of pulping time. The ethanol concentration displays a low influence. The tensile index values then are higher at high temperature, high ethanol concentration, and short pulping time.

## 4. Conclusions

The chemical characteristics of *Paulownia fortunei* wood (abbreviated simply as Paulownia) are similar, in regard to holocellulose, lignin, glucan, xylan, araban, and acetyl groups, to other raw materials used in the autohydrolysis and pulping process. Thus, Paulownia wood could be a suitable raw material for autohydrolysis treatment and pulp and paper making. From autohydrolysis, a valuable liquid phase could be obtained. The highest increment of xylooligomer content has been observed at 180−200 °C. The optimum of solubilized components has been obtained at 190 °C (0.92 g/L glucose, 1.61 g/L xylose, 0.60 g/L arabinose, 0.93 g/L acetic acid, 0.047 g/L 5-hydroxymethylfurfural, 0.141 g/L furfural, and 14.66 g/L oligomers).

Pulping temperature has a high influence on the greater number of dependent variables, except for lignin content. An increase in pulping temperature has a positive effect on the kappa number, glucan and lignin content, and tensile index values. However, it has a negative effect on the yield.

In conclusion, low ethanol concentration (20%−30%), high temperature (180 °C), and short pulping time (30 min) should be applied to produce cellulose pulp from Paulownia wood using an ethanol−soda process. Under those operation conditions, the yield is ~40%, which is sensibly higher than the minimum values (~32%) that are observed under the most-severe operation conditions.

## Acknowledgment

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# HYDROTHERMAL AND ETHANOL-WATER PULPING OF *Arundo donax* L. CANE. A PRELIMINARY STUDY.

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Scientific Topic: Sustainable Development, Risk Analysis and Environmental Impact

*Arundo donax* L., is a perennial, herbaceous plant of the Graminae family. Utilization of this plant as possible bio-source for energy generation and/or for pulp in the paper industry has been analyzed due to its high potential for biomass production [1,2,3].

On the other hand, autohydrolysis, based on the utilization of water as sole fractionation agent, could origin a selective solubilisation of hemicelluloses, leading to liquors containing sugar oligomers, sugars and sugar-decomposition products and to a solid phase, which could be subjected to further processing as pulp and paper process. Under this way, *Arundo donax* L. fibers coming from the hydrothermal treatment may represent an interesting alternative to wood fibres. Non isothermal autohydrolysis processing of wood chips from *Arundo donax* L. was performed at operation temperature of 185 °C and solid water ratio of 1/8 to ensure minimum cellulose fibre degradation. (Table 1).

Table 1. Raw material and solid phase composition from non isothermal autohydrolysis (ASP) of *Arundo donax* (g/100 g processed solids).

| | Glucan | Xylan | Arabian | Acetyl groups | Holocellulose | lignin |
|---|---|---|---|---|---|---|
| Raw material | 34.77 | 19.42 | 1.55 | 3.42 | 59.16 | 24.22 |
| *ASP* | 39.09 | 20.62 | 0.91 | 3.65 | 63.27 | 26.58 |

In addition, an organosolv pulping process was used to study the pulp characteristics from the solid fraction after hydrothermal treatment (Table 2). Organosolv pulping process was performed at operation temperature of 200 °C, processing time of 130 min, ethanol concentration of 60% (weight concentration) and solid water ratio of 1/8.

Table 2. Properties of organosolv pulps from *Arundo donax* L (% on oven-dry pulp).

| | AT** | Raw material | | AT** | Raw material |
|---|---|---|---|---|---|
| Yield (%) | 41.36 | 38.24 | Acetyl groups (%) | 0.69 | 0.45 |
| Kappa number | 38.75 | 53.50 | Xylan (%) | 12.89 | 8.76 |
| Viscosity (ml $g^{-1}$) | 729.32 | 870.71 | Holocellulose (%) | 84.63 | 77.71 |
| Glucan (%) | 71.05 | 68.50 | Klason lignin (%) | 8.68 | 12.11 |

**AT= the solid fraction after non isothermal autohydrolysis treatment.

Comparing the pulps obtained under both process (after hydrothermal pretreatment and without pretreatment), a higher yield, xylan, acetyl groups and holocellulose of solid phase are observed, glucan is similar and lower value in Klason lignin is found. The viscosity value obtained after hydrothermal pretreatment are lower than that without pretreatment.

The ethanol–water pulping could be an adequate process for solid residues from hydrothermal treatment of *Arundo donax* L. Under selected operation conditions, similar characteristics after hydrothermal pretreatment with respect to without pretreatment pulps are found.

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# PRODUCCIÓN DE PASTA DE CELULOSA A PARTIR DE TALLOS DE GIRASOL

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## RESUMEN

En este trabajo se evalúa la adecuación de los tallos de girasol como materia prima para la producción de pasta de celulosa. En primer lugar se ha analizado la composición de los tallos de girasol, para a continuación realizar estudios de pasteo por los procesos Kraft y sosa-antraquinona, encontrándose que con ambos procesos es posible conseguir pasta de celulosa con un alto contenido en holocelulosa y un bajo contenido en lignina. De los datos se desprende que el proceso a la sosa-antraquinona produce una pasta de mejores características químicas.

A continuación se ha estudiado el pretratamiento hidrotérmico, evaluando el grado de fraccionamiento conseguido, la composición y pureza de la fase líquida. Se encuentra que el óptimo es el experimento llevado a cabo con una temperatura máxima de 190º C, donde la fase líquida contiene 14.4 g oligosacáridos/100 g materia prima, representando el 62% de los sólidos disueltos en la fase líquida.

Por último se ha realizado un pasteo con mezclas de etanol-agua sobre el residuo sólido del pretratamiento hidrotérmico, encontrándose rendimientos entre 41.5 y 65.3 g/100 g materia prima, del mismo orden que los de los procesos Kraft y NaOH-AQ. Se ha procedido a realizar un refinado de algunas pastas etanol-agua y a continuación se han medido las propiedades físicas del papel resultante, encontrándose que son del mismo orden que las obtenidas para otros materiales y otros procesos, confirmando la validez de la producción simultánea de oligosacáridos y papel.

## PALABRAS CLAVE

Pasta celulósica, papel, pretratamiento hidrotérmico, residuos agrícolas, girasol, organosolv.

## INTRODUCCIÓN

La producción mundial de pastas celulósicas ha aumentado mucho en los últimos años, y se prevén tasas de crecimiento en la demanda de papel del orden del 3% anual (Casey, 1990). La gran mayoría del papel se produce a partir de madera. Resulta interesante la búsqueda de materias primas en la producción de papel que sean alternativas a la madera.

En el caso de que se aprovechen materiales lignocelulósicos de origen residual se consigue un doble efecto: el beneficio ecológico, al eliminar una fuente de contaminación, y el factor económico, al dotar al material de un valor añadido que no tiene como tal residuo. En España, dada su fuerte actividad agrícola, la generación de residuos es especialmente elevada, produciéndose anualmente del orden de $2 \cdot 10^7$ toneladas (Jiménez y col., 1991a). La economía del proceso es más favorable cuando los residuos aparecen concentrados geográficamente (como es el caso de los residuos del cultivo de algodón en la comunidad andaluza, según Jiménez y col., 1991b), al eliminarse los costes de recolección y transporte, que pueden ser muy significativos en este tipo de procesos (Vázquez y col., 1991).

Un material que cumple estas características son los tallos de girasol. En España se producen anualmente $1.3 \cdot 10^9$ kg/año de girasol y aproximadamente una tercera parte en Andalucía. Esto genera una gran cantidad de residuos lignocelulósicos, destacando los de tallos de girasol, que actualmente se queman. El aprovechamiento de estos tallos para la producción de pasta de celulosa generaría el doble beneficio anteriormente mencionado.

En este trabajo se evalúa la adecuación de los tallos de girasol como materia prima para la producción de pasta de celulosa. En primer lugar se ha analizado la composición de los tallos de girasol, para a continuación realizar estudios de pasteo por procedimientos convencionales, como el kraft, y por procesos menos contaminantes como son el pasteo a la NaOH-antraquinona y el pasteo organosolv (con etanol como disolvente orgánico).

En el pasteo organosolv se puede realizar con anterioridad una etapa de tratamiento hidrotérmico del material, con el fin de sacar provecho a la fracción hemicelulósica. Estos tratamientos, también denominados autohidrólisis, consisten en someter una suspensión acuosa del material lignocelulósico a la acción del calor, con temperaturas máximas en el intervalo 150-220º C. La acción de los protones, provenientes en primera instancia del agua y después de la hidrólisis de los grupos acetilo del material, solubiliza selectivamente las hemicelulosas en forma de oligosacáridos, dejando un residuo sólido compuesto mayoritariamente por celulosa y lignina, apto para otros tratamientos, como la producción de pasta celulósica (Garrote y col., 1999). El compuesto mayoritario que cabe esperar que se encuentre en la fase líquida son oligosacáridos. Estos compuestos presentan un valor añadido por ser aditivos alimentarios, de tal modo que la producción de los mismos conjuntamente con la pasta celulósica aumentaría el rendimiento económico y ecológico del proceso global de aprovechamiento.

## EXPERIMENTAL

Materia prima: Tallos de girasol, secados al sol y deshojados en los propios terrenos de cultivo, se trituraron en un molino de martillo y se separó la médula, utilizándose para todos los experimentos de pasteado la fracción desmedulada. Mediante un posterior tamizado se seleccionó la fracción con tamaños de partícula comprendidos entre 10 y 20 mm.

Caracterización de la materia prima: La materia prima se sometió a diversos protocolos analíticos para conocer su composición. Estos protocolos fueron los siguientes:

- Solubilidad en agua caliente (TAPPI 257).
- Solubilidad en sosa al 1% (TAPPI 212).
- Extraíbles con etanol-benceno (TAPPI 204).
- Holocelulosa (método de Wise).
- $\alpha$-celulosa (TAPPI 203-OS-61).
- Lignina (TAPPI 222).

Análisis de las pastas y de las hojas de papel: Las pastas se sometieron a análisis similares a los de la materia prima y a medidas de rendimiento (TAPPI 257) y a las hojas se les midió el alargamiento (UNE 57054), el índice de tracción (UNE 57054), el índice de rotura (UNE 57058) y el índice de desgarro (UNE 57-033-86).

Pasteado: Se han realizado experimentos de pasteado mediante tres procesos diferentes:

1. Proceso Kraft: Los experimentos se llevaron a cabo utilizando un reactor cilíndrico discontinuo de 15 L de capacidad, calentado mediante resistencias eléctricas y unido a un módulo de control que permite el giro continuo del reactor. Las variables independientes seleccionadas en el pasteo Kraft han sido la concentración de álcali (entre el 10 y el 20%), la sulfidez (entre el 20 y el 30%), la relación líquido/sólido (entre 6 y 10 g líquido/g girasol), la temperatura de pasteo (entre 125 y 175º C) y el tiempo de pasteo (entre 1 y 2 h). Al final de los experimentos, la pasta se separó de los licores negros mediante filtración a través de un tamiz de 0.16 mm de luz y se lavó con agua. Posteriormente la pasta se desintegró a 1200 rpm durante 30 min, se desfibró en un refinador Sprout-Waldron y se separaron los incocidos en un filtro Strainer de 0.4 mm de luz.

2. Proceso Sosa-antraquinona: Los experimentos se llevaron a cabo en el mismo reactor que se utilizó para el proceso Kraft. Las variables seleccionadas en el proceso a la sosa-AQ fueron la concentración de NaOH (entre 5 y 15%), la concentración de antraquinona (entre 0 y 0.1%), la relación líquido/sólido (entre 4 y 8 g líquido/g girasol), la temperatura de pasteo (entre 125 y 175º

C) y el tiempo de pasteo (entre 0.5 y 1.5 h). Al final de los experimentos, la pasta se trató de modo similar al llevado a cabo en el proceso Kraft.

3. Proceso organosolv:
    a. *Pretratamiento hidrotérmico*: la materia prima y el agua se mezclaron para obtener un hidromódulo de 6 g agua/g materia prima, en base seca, y se introdujeron en un reactor Berghof de acero inoxidable de 1 L de volumen total, equipado con agitador y sistema de control de temperatura. La suspensión se calentó siguiendo el perfil de calentamiento estándar del reactor hasta llegar a temperaturas máximas en el intervalo de 165 a 200º C y se enfrió. Al alcanzar temperatura ambiente, el reactor se abrió y las fases sólida y líquida se separaron mediante filtración. El sólido se lavó con agua y se utilizó para determinar el rendimiento del pretratamiento y la fase líquida se analizó para conocer su composición. Una alícuota se filtró a través de una membrana de acetato de celulosa de 0.45 $\mu$m de diámetro de poro y se analizó mediante cromatografía líquida de alta resolución (Garrote y col., 1999) para conocer su contenido en glucosa, xilosa, arabinosa, ácido fórmico, ácido acético, hidroximetilfurfural y furfural. Una segunda alícuota se sometió a posthidrólisis con ácido sulfúrico (4% $H_2SO_4$, 40 min, 121º C) y se analizó mediante cromatografía líquida de alta resolución para, mediante el aumento de la concentración de los azúcares, medir el contenido en oligosacáridos (Garrote y col., 1999). Otra alícuota de la fase líquida se utilizó para determinar la fracción solubilizada durante el pretratamiento, secándola a 105º C hasta peso constante y realizando los correspondientes balances de materia.
    b. *Proceso organosolv*: el residuo sólido procedente del pretratamiento hidrotérmico se sometió a un proceso de pasteo con mezclas etanol/agua en el reactor Berghof mencionado anteriormente. Este residuo se guardó húmedo, con el fin de simular más adecuadamente un proceso industrial, el contenido en humedad varió entre el 60 y el 80%. La relación líquido/sólido se fijó en 10 g disolución/g residuo sólido, considerando la humedad de residuo como agua. Las variables seleccionadas en el proceso organosolv fueron la concentración de etanol (entre 40 y 70%), la temperatura de pasteo (entre 145 y 175º C) y el tiempo de pasteo (entre 40 y 120 min). Después del pasteado se separó la fase líquida de los licores de cocción, que se guardaron para su posterior análisis de la fase líquida, de modo similar al realizado para la fase líquida del pretratamiento hidrotérmico. La pasta se lavó con una disolución de etanol (de la misma concentración que la utilizada en el pasteo y doble volumen) y después se desintegró (20 min a 1200 rpm) y finalmente se lavó con agua destilada.

Diseño experimental: para la selección de los experimentos a realizar en cada proceso se utilizó un diseño central compuesto, en el caso del pasteo Kraft y en el NaOH-AQ, que permite calcular la influencia de las cuatro variables independientes sobre las distintas variables dependientes como un polinomio de segundo orden, realizándose 27 experimentos para cada pasteo, al considerarse cinco variables independientes. En el caso del proceso organosolv, con tres variables independientes, se utilizó un diseño cuadrado latino, a cuatro niveles para las tres variables, con un total de 16 experimentos.

Para facilitar la comparación directa de los coeficientes obtenidos al ajustar cada variable dependiente mediante el polinomio de segundo orden, se procedió a normalizar la variación de las variables independientes en el intervalo –1 a +1 mediante la siguiente ecuación:

$$X_N = 2 \cdot \frac{x - \bar{x}}{x_{MAX} - x_{MIN}}$$

donde $X_N$ es el valor normalizado de la variable independiente x, $\bar{x}$ es el valor medio de dicha variable y $x_{MAX}$ y $x_{MIN}$ son los valores máximo y mínimo de dicha variable.

Refino de las pastas: Las pastas obtenidas mediante organosolv se sometieron a un proceso de refino en una pila Valley (0.5% de consistencia durante 5 min). El grado de refino se ha medido como índice Shopper-Riegler (UNE 57-025).

Formación de hojas: Hojas de papel se obtuvieron utilizando un formador de hojas ENJO-F-39.71 siguiendo metodología estándar (UNE 57042-74).

## RESULTADOS

Composición de la materia prima: En la tabla 1 se muestra la caracterización química de la materia prima, tanto de los tallos de girasol tal cual se recogen, como de la médula y de la fracción desmedulada. Es esta última la utilizada en todos los experimentos. La médula supone solamente un 7% en peso del total de los tallos.

Se ve que los valores de las solubilidades en agua caliente y en sosa al 1% y los extraíbles en etanol-benceno son similares a las de otros residuos agrícolas, como los tallos de sorgo o las pajas de algunos cereales, pero superior al de maderas típicamente madereras como el eucalipto. En cuanto a los componentes estructurales, vemos que los tallos de girasol presentan contenidos en holocelulosa y $\alpha$-celulosa similares a otros residuos agrícolas e inferiores al eucalipto, mientras que el contenido en lignina es bastante bajo. Si nos fijamos en la fracción desmedulada, la utilizada en los experimentos, vemos que los contenidos en solubles y extraíbles son menores, aumentando el contenido en los componentes estructurales.

Procesos Kraft y NaOH-antraquinona: estos dos procesos se han llevado a cabo para comprobar la viabilidad de la producción de pasta celulósica a partir de los tallos de girasol. En las tablas 2 se muestran los intervalos de variación y los valores medios de las distintas magnitudes medidas en los procesos Kraft y a la NaOH-AQ.

A la vista de los datos presentados en la tabla 2, vemos que se puede obtener pasta celulósica con ambos procesos, pareciendo más apto el proceso a la sosa-antraquinona, al presentar siempre mejores resultados que el proceso Kraft. Analizando los datos de rendimiento y composición de pasta celulósica, podemos decir que debería ser mejor aquella pasta con mayor contenido en holocelulosa y menor contenido en lignina. También resulta interesante, desde un punto de vista económico, rendimientos elevados. Si atendemos a los valores medios, vemos que el proceso NaOH-AQ presenta un mayor rendimiento del proceso (54.1% frente a 45.2%), mayores contenidos en holocelulosa (79.3 frente a 68.4) y menores contenidos en lignina (20.4 frente a 23.1).

Si atendemos a los mejores resultados obtenidos con cada proceso, podemos seleccionar como pasta Kraft óptima la obtenida con las siguientes condiciones de operación: concentración de álcali: 20%, sulfidez: 30%, relación líquido/sólido: 10 g líquido/g girasol, temperatura de pasteo: 125ºC) y tiempo de pasteo: 1 h. En el proceso NaOH-AQ la pasta óptima sería la obtenida con una concentración de NaOH: 15%, concentración de AQ: 0.1%, relación líquido/sólido: 8 g líquido/g girasol, temperatura de pasteo: 175º C y tiempo de pasteo: 1.5 h. Bajo estas condiciones óptimas de nuevo resulta mejor el proceso NaOH-AQ, al presentar un considerablemente mayor rendimiento (41.3% frente a 33.8%), mayor contenido en holocelulosa (95.8 frente a 78.2) y menor contenido en lignina (5.4 frente a 9.9).

Pretratamiento hidrotérmico:

Para estudiar la influencia del pretratamiento hidrotérmico, se realizaron distintas experiencias de autohidrólisis en condiciones no isotermas, llegando a temperaturas máximas de 160-200º C. En estos experimentos se midió el grado de fraccionamiento de la materia prima, poniendo especial énfasis en la fase líquida, estudiando su cantidad, composición y pureza.

En la tabla 3 se muestran los datos de rendimiento, fracción solubilizada y pérdidas de los tratamientos hidrotérmicos. Las pérdidas se calculan mediante balances de materia y estarían compuestas fundamentalmente por productos volátiles. Se observa que el rendimiento baja de modo continuo hasta valores de 72.5%, mientras que la fracción solubilizada presenta su valor máximo a 190ºC con 23.2%. Las pérdidas son de pequeña importancia.

En la tabla 4 se muestran las concentraciones de los distintos compuestos analizados en la fase líquida. Se observa que el compuesto mayoritario, como era de prever, son los oligosacáridos, con concentraciones máximas de 26.9 g/L a 190º C, para después decrecer. Se observa que los compuestos derivados de las hemicelulosas (oligosacáridos, xilosa, arabinosa y ácidos acético y fórmico) presentan la tendencia de aumentar su concentración con la temperatura.

Si realizamos los correspondientes balances de materia, vemos que en las condiciones cercanas al óptimo los oligosacáridos representan el 61% en peso de la fracción solubilizada que se expone en la tabla 3 a 180º C, el 62% a 190º C y el 58% a 200º C. Esto indica que trabajando en condiciones cercanas al óptimo de oligosacáridos se obtiene una fase líquida compuesta aproximadamente en un 60% por oligosacáridos. También se puede calcular que estos oligosacáridos representan entre el 11.3 y el 14.4 % de la materia prima inicial, lo que indica que en este pretratamiento hidrotérmico se puede conseguir entre el 10-15% de la materia prima en forma de oligosacáridos, siendo el resto de la fase líquida, del orden del 2-3%, compuestos provenientes de la degradación de azúcares y de solubilización de la lignina.

Proceso organosolv:

Sobre el residuo sólido del pretratamiento hidrotérmico se llevó a cabo un estudio de deslignificación mediante un proceso organosolv. En primer lugar se seleccionó el tratamiento hidrotérmico llevado a cabo a 180º C, ya que en él se obtenían cerca del 80% del máximo de oligosacáridos (en concreto 11.4 g oligosacáridos/100 g materia prima) y las condiciones de operación son más suaves que las del máximo de oligosacáridos. Esto se lleva para prevenir que, a condiciones de operación más severas, el pretratamiento ataque a la fracción celulósica, rompiendo parcialmente su estructura y provocando que se obtengan pastas de menor viscosidad (Garrote y col., 2003).

En la tabla 5 se muestran las condiciones de operación ensayadas y el fraccionamiento obtenido. Las tres fracciones medidas son el rendimiento en sólido, la fracción solubilizada y las pérdidas (medidas por diferencia), todas referidas a la misma base de cálculo, el residuo sólido. Hay que tener en cuenta que el rendimiento del pretratamiento hidrotérmico a 180º C es del 78.0%. Así, si nos referimos al rendimiento, vemos que éste varía entre 41.5 y 65.3%, con valores medios de 51.8%, respecto a la materia prima. El rendimiento en sólido es mayor que en el proceso Kraft (45.2%) y algo menor que en el proceso NaOH-AQ (54.1%), pero al aprovechar también los oligosacáridos, la fracción de materia prima “valorizada” es de 63.2% (en valores medios), casi dos terceras partes del material. En cuanto a la fracción solubilizada en forma de “lejías negras”, varía entre 6.4 y 23.0 g/100 g materia prima, con valores medios de 13.5 g, y está compuesta fundamentalmente por fragmentos de lignina solubilizada y derivados de polisacáridos.

Para comprobar la viabilidad de la producción de papel mediante la combinación de autohidrólisis-organosolv, se procedió a refinar algunas pastas y a medir las propiedades físicas de las hojas resultantes, datos que se muestran en la tabla 6. Se ve que se obtiene un grado de refino elevado, entre 38.3 y 59.8 ºSR, con buenas propiedades físicas de las hojas, del mismo orden que las encontradas con otros residuos agrícolas como la paja de trigo en procesos etanol-agua (Jiménez y col., 2004) y etanol-acetona (Jiménez y col., 2002), lo que confirma la validez del proceso propuesto para la producción conjunta de oligosacáridos y papel.

## CONCLUSIONES

La composición química de los tallos de girasol es similar a la de otros residuos agrícolas y parece apta para la producción de pasta celulósica.

Es viable la producción de pasta de celulosa a partir de tallos de girasol tanto mediante el proceso Kraft como mediante el proceso sosa-antraquinona, siendo más prometedor este último, en cuanto al rendimiento y contenidos en holocelulosa y lignina de las pastas, tanto si se estudian los valores medios de dichas variables como los experimentos óptimos de cada proceso.

En el pretratamiento hidrotérmico se obtienen candidades elevadas de oligosacáridos, hasta el 14.4% de la materia prima inicial, con una pureza aceptable. La posterior aplicación comercial de estos compuestos necesitaría etapas de purificación y refino. En el proceso etanol-agua llevado a cabo sobre el residuo sólido del pretratamiento se han obtenido valores de rendimiento similares a los del proceso Kraft y NaOH-AQ. Después del refino, las propiedades físicas de las hojas resultantes han resultado del mismo orden que las halladas por otros autores para materiales y procesos similares.

Es posible la producción secuencial de oligosacáridos (entre 10-15%) y papel (entre 41.5 y 65.3%), logrando así un mayor aprovechamiento de la materia prima y una menor cantidad de residuos.

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**Tabla 1**
**Composición química de los tallos de girasol (% en peso en base seca)**

| | Muestra inicial | Tallos desmedulados | Médula |
|---|---|---|---|
| **Solubles en agua caliente** | 21.1 | 20.4 | 25.5 |
| **Solubles en sosa al 1%** | 50.4 | 42.2 | 55.6 |
| **Extraíbles en etanol-benceno** | 4.38 | 3.65 | 3.14 |
| **Holocelulosa** | 66.9 | 74.2 | 64.5 |
| **$\alpha$-celulosa** | 37.6 | 39.3 | 34.6 |
| **Lignina** | 10.8 | 13.5 | 4.18 |

**Tabla 2**
**Resultados experimentales de la caracterización de las pastas obtenidas en los procesos Kraft y NaOH-antraquinona**

| | Kraft | | | NaOH-antraquinona | | |
|---|---|---|---|---|---|---|
| | Máximo | Mínimo | Medio | Máximo | Mínimo | Medio |
| **Rendimiento** | 31.7 | 72.1 | **45.2** | 40.6 | 70.9 | **54.1** |
| **Holocelulosa** | 61.0 | 80.9 | **68.4** | 69.5 | 95.8 | **79.3** |
| **$\alpha$-celulosa** | 61.4 | 73.7 | **66.5** | n. d. | n. d. | **n. d.** |
| **Lignina** | 9.91 | 29.7 | **23.1** | 5.40 | 32.5 | **20.4** |

n. d.: no determinado

## Tabla 3
## Fracciones recuperadas en el tratamiento hidrotérmico

| Temperatura (ºC) | Rendimiento (g/100 g materia prima) | Fracción solubilizada (g/100 g materia prima) | Pérdidas (g/100 g materia prima) |
|---|---|---|---|
| 160 | 86.4 | 14.5 | -0.9 |
| 165 | 84.8 | | |
| 170 | 81.2 | 16.5 | 2.3 |
| 175 | 80.3 | | |
| 180 | 78.0 | 18.4 | 3.6 |
| 190 | 73.7 | 23.2 | 3.1 |
| 200 | 72.5 | 21.8 | 5.7 |

## Tabla 4
## Composición de la fase líquida obtenida en el tratamiento hidrotérmico (concentraciones en g/L)

| **Temperatura (ºC)** | 165 | 170 | 175 | 180 | 185 | 190 | 200 |
|---|---|---|---|---|---|---|---|
| **Oligosacáridos** | 9.5 | 11.3 | 13.6 | 21.0 | 24.2 | 26.9 | 23.3 |
| **Glucosa** | 0.5 | 0.6 | 1.2 | 0.8 | 1.2 | 1.0 | 0.7 |
| **Xilosa** | 1.3 | 1.6 | 1.7 | 2.0 | 1.9 | 2.6 | 2.1 |
| **Arabinosa** | 0.0 | 0.1 | 0.2 | 0.3 | 0.5 | 0.6 | 0.6 |
| **Ácido fórmico** | 0.2 | 0.3 | 0.3 | 0.4 | 0.8 | 0.8 | 1.0 |
| **Ácido acético** | 0.4 | 0.5 | 1.0 | 1.1 | 2.4 | 2.4 | 4.6 |
| **Hidrometifurfural** | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 0.1 |
| **Furfural** | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |

## Tabla 5
## Fracciones recuperadas en el proceso organosolv

| Temperatura (º C) | Etanol (%) | Tiempo (min) | Rendimiento (%) | Fracción solubilizada (%) | Pérdidas (%) |
|---|---|---|---|---|---|
| 145 | 50 | 40 | 83.7 | 12.2 | 4.1 |
| 155 | 70 | 40 | 69.3 | 8.2 | 22.5 |
| 165 | 40 | 40 | 65.8 | 20.2 | 14.0 |
| 175 | 60 | 40 | 60.4 | 15.1 | 24.5 |
| 145 | 70 | 67 | 78.4 | 8.7 | 12.9 |
| 155 | 50 | 67 | 73.1 | 15.7 | 11.2 |
| 165 | 60 | 67 | 67.6 | 16.0 | 16.5 |
| 175 | 40 | 67 | 53.2 | 29.5 | 17.3 |
| 145 | 60 | 93 | 70.8 | 9.4 | 19.8 |
| 155 | 40 | 93 | 64.3 | 21.6 | 14.1 |
| 165 | 70 | 93 | 62.6 | 15.9 | 21.5 |
| 175 | 50 | 93 | 54.2 | 28.3 | 17.5 |
| 145 | 40 | 120 | 71.3 | 16.7 | 11.9 |
| 155 | 60 | 120 | 60.6 | 15.5 | 23.9 |
| 165 | 50 | 120 | 62.0 | 22.3 | 15.8 |
| 175 | 70 | 120 | 65.6 | 21.7 | 12.7 |

## Tabla 6
## Propiedades físicas de las hojas de papel obtenidas mediante autohidrólisis-organosolv

| Temperatura (º C) | Shopper Riegler (ºSR) | Longitud de ruptura (m) | Alargamiento (%) | Índice de estallido (kN/g) | Índice de desgarro (N·m$^2$/kg) |
|---|---|---|---|---|---|
| 145 | 49,5 | 2377 | 1.09 | 0.97 | 1.29 |
| 155 | 38,3 | 2463 | 1.57 | 1.17 | 1.57 |
| 165 | 39,8 | 2823 | 1.53 | 1.48 | 2.01 |
| 175 | 56,5 | 2757 | 1.95 | 1.90 | 2.53 |
| 145 | 59,8 | 2228 | 1.23 | 0.87 | 1.61 |
| 155 | 56.0 | 2824 | 1.78 | 1.36 | 1.55 |