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CHEMICAL TRANSFORMATIONS OF FAST-GROWING POPLAR WOOD DURING THERMAL MODIFICATION AND THEIR RELATION TO HYGROSCOPICITY AND DIMENSIONAL STABILITY

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Abstract. Thermal modification upgrades non-durable timber without biocides, but the process is still specified as a temperature and time schedule rather than as a set of chemical reactions with known extents. This article reviews the reaction network that operates in the wood cell wall between 160 and 220 °C, namely deacetylation of glucuronoxylan, autocatalytic hydrolysis of glycosidic bonds by the liberated acetic acid, dehydration of pentoses to furfural with subsequent furanic polymerisation, and cleavage followed by recondensation of lignin. It then proposes an experimental programme in which each reaction extent is quantified independently on fast-growing poplar and correlated with accessible hydroxyl concentration, equilibrium moisture content, anti-swelling efficiency and bending strength.

Keywords: wood chemistry; Populus; thermal modification; deacetylation; autohydrolysis; furfural; lignin condensation; hydroxyl accessibility; sorption isotherm.

Аннотация. Термическая модификация повышает долговечность древесины с низкой естественной стойкостью без использования биоцидов, однако данный процесс до сих пор в основном задаётся режимами температуры и времени, а не набором химических реакций с известной степенью протекания. В данной статье рассматривается сеть реакций, происходящих в клеточной стенке древесины при температуре 160–220 °C, включая деацетилирование глюкуроноксила, автокаталитический гидролиз гликозидных связей под действием высвобождающейся уксусной кислоты, дегидратацию пентоз с образованием фурфурола с последующей фурановой полимеризацией, а также расщепление и последующую реконденсацию лигнина. Далее предлагается экспериментальная программа, в рамках которой степень протекания каждой реакции будет количественно определяться независимо на быстрорастущей древесине тополя и сопоставляться с концентрацией доступных гидроксильных групп, равновесной влажностью, эффективностью против разбухания и прочностью при изгибе.

Ключевые слова: химия древесины; *Populus*; термическая модификация; деацетилирование; автогидролиз; фурфурол; конденсация лигнина; доступность гидроксильных групп; изотерма сорбции.

Annotatsiya. Termik modifikatsiya biologik chidamliligi past bo‘lgan yog‘ochning xususiyatlarini biotsidlardan foydalanmasdan yaxshilaydi, biroq ushbu jarayon hali ham reaksiyalarning ma’lum darajadagi borishi asosida emas, balki asosan harorat va vaqt rejimlari orqali belgilanadi. Ushbu maqolada 160–220 °C oralig‘ida yog‘och hujayra devorida sodir bo‘ladigan reaksiyalar tarmog‘i ko‘rib chiqiladi. Jumladan, glukuronoksilanning deatsetillanishi, ajralib chiqadigan sirka kislota ta’sirida glikozid bog‘larining avtokatalitik gidrolizi, pentozalarning degidratatsiyasi natijasida furfurool hosil bo‘lishi va undan keyingi furanik polimerlanish, shuningdek, ligninning parchalanishi va keyinchalik qayta kondensatsiyalanishi tahlil qilinadi. Shuningdek, har bir reaksiyaning borish darajasini tez o‘svuchi terak yog‘ochida mustaqil ravishda miqdoriy aniqlash hamda ularni mavjud gidroksil guruhlarini konsentratsiyasi, muvozanat namligi, shishishga qarshi samaradorlik va egilishdagi mustahkamlik bilan bog‘lashga qaratilgan eksperimental dastur taklif etiladi.

Kalit so‘zlar: yog‘och kimyosi; *Populus*; termik modifikatsiya; deatsetillanish; avtogidroliz; furfurool; ligninning kondensatsiyalanishi; gidroksil guruhlarining mavjudligi; sorbsiya izotermasi.

INTRODUCTION. Fast-growing poplar and willow dominate the plantation timber resource of Central Asia, and they are poor material. Low density, high hygroscopicity and negligible natural durability confine them to pallets, packaging and low-grade panel furnish, while construction and joinery timber is imported. Raising the value of this resource does not require a new species; it requires changing the chemistry of the wood already available [12, 18].

Thermal modification is the most industrially mature route to that end. Heating timber above roughly 160 °C under limited oxygen access lowers equilibrium moisture content, improves dimensional stability and raises decay resistance without introducing any biocide, which matters in a regulatory climate that keeps narrowing the permitted list of wood preservatives [5, 19, 26]. Commercial processes differ mainly in the medium and in whether the reactor is vented or sealed, and the technology is well established in Europe and increasingly elsewhere [17, 24], with life-cycle and weathering assessments of the resulting material now available [4, 10].

The chemistry underlying it is understood in outline. O-acetyl groups on glucuronoxylan hydrolyse first, releasing acetic acid; the acid lowers the pH of the cell wall water and catalyses cleavage of glycosidic bonds, so the hemicelluloses depolymerise well before cellulose is affected [9, 21]. Liberated pentoses dehydrate to furfural, which polymerises into a dark, water-repellent furanic network distributed through the treated wood [23]. Lignin undergoes both β -O-4 cleavage and recondensation into carbon-carbon linked

structures. Cellulose crystallinity rises apparently, largely because amorphous material is preferentially lost rather than because crystallites grow.

What remains unsettled is the link between these reactions and the property changes they are supposed to explain. The reduction in hygroscopicity is routinely attributed to the loss of accessible hydroxyl groups, yet several careful studies report only weak correlation between accessible hydroxyl concentration and equilibrium moisture content, which implies that matrix stiffening and crosslinking contribute independently [7, 14, 25, 27]. The debate is not academic: if crosslinking dominates, then process routes that maximise furanic network formation are preferable to those that simply maximise mass loss, and the strength penalty can be reduced. Compounding this, almost all mechanistic work has been done on beech, spruce, Scots pine and eucalypt. Poplar, with its syringyl-rich lignin and its high xylan acetyl content, has a different starting chemistry and cannot be assumed to follow the same course.

This article addresses that gap conceptually. Its objectives are to set out the reaction network operating in poplar between 160 and 220 °C from published evidence; to propose an experimental design in which the extent of each reaction is measured separately rather than inferred from mass loss alone; and to define the analytical protocol that would allow reaction extents to be correlated with hygroscopic and mechanical response.

MATERIALS AND METHODS

Sources were retrieved from Scopus, Web of Science Core Collection and ScienceDirect. Search strings paired a process term (thermal modification, heat treatment, hydrothermal, torrefaction) with a chemical term (deacetylation, autohydrolysis, glucuronoxylan, furfural, lignin condensation, hydroxyl accessibility) and, where relevant, a substrate term (*Populus*, poplar, hardwood). Coverage ran from 2015 onward with priority given to 2021 to 2026 material; older work was kept only where it defines a method or reports a mechanism that has not been superseded. Papers were retained when they reported a quantified chemical change alongside a measured physical property, and excluded when only colour or mass loss was given.

Structural characterisation combines ATR-FTIR, following the carbonyl band near 1735 cm⁻¹ attributable to acetyl and uronic ester groups and the aromatic skeletal bands near 1595 and 1505 cm⁻¹, with solid-state ¹³C CP/MAS NMR and X-ray diffraction. Crystallinity is reported both by the Segal peak-height method [20] and by full-profile deconvolution, since the two disagree systematically and quoting only the former has caused confusion in this literature.

Hygroscopic behaviour is the linking measurement. Accessible hydroxyl concentration is determined gravimetrically by deuterium exchange in a dynamic vapour sorption apparatus, following the protocol parameters established for sample mass, exposure time and drying rate [26]. Sorption isotherms are recorded over 0 to 95 % relative humidity in adsorption and desorption, and analysed with the Hailwood-Horrobin model to separate monolayer from polylayer contributions and to quantify hysteresis [13, 22]. Anti-swelling efficiency is computed from radial and tangential swelling between oven-dry and water-saturated states, and bending strength and stiffness follow ISO 13061-3 and ISO 13061-4.

Reaction extents and physical responses are then related by correlation and partial least squares analysis of the full variable set given in Table 1.

RESULTS AND DISCUSSION

No wood has been treated by the author at this stage. This section assembles the published evidence that defines the expected behaviour and, more importantly, identifies the point at which that evidence becomes contradictory.

The primary reaction sequence is well supported. Hydrothermal treatment of eucalypt showed that acetyl groups are cleaved from both xylan and its degradation oligomers, and that the resulting acetic acid concentration governs the hydronium ion supply that drives subsequent hydrolysis [9]; modelling of proton evolution during autohydrolysis confirms that a steady-state proton concentration is set by the initial acetyl content and the neutralising capacity of the ash [21]. In birch, formic and acetic acid concentrations formed during hydrothermal treatment correlate with the resulting colour, strength and hardness [23], and infrared analysis of cell-wall components isolated from thermally modified beech confirms deacetylation as the leading change [6]. Comparison of open and closed reactor systems on eucalypt demonstrated that hygroscopicity changes differ between the two, and that part of the change is reversible [28], which is direct evidence that retaining the acid matters.

The furanic pathway has been characterised more recently. Solid-state ^{13}C NMR and MALDI-ToF analysis of heat-treated beech and fir showed that hydrophobicity develops mainly through furanic moieties generated from hemicellulose degradation in the acid environment created by acetyl hydrolysis, with furfural polymerising to insoluble, dark, water-repellent resins whose contribution grows strongly between 200 and 300 °C [20]. This provides a chemical mechanism for water repellency that is independent of hydroxyl loss.

The contradiction lies in the sorption data. Accessible hydroxyl content falls steadily with treatment temperature, and hygroscopicity falls alongside it [14]. Yet studies that measure both quantities on the same material report poor correlation between them, and wet-processed thermally modified timber subjected to post-treatment leaching shows further changes in sorption and dimensional stability without any further change in accessible hydroxyl content [14, 27]. Work on hot-water-extracted spruce separated the two effects explicitly [2]: extraction reduced sorption by removing amorphous carbohydrates and hydroxyl sites, whereas thermal modification reduced sorption additionally through matrix crosslinking and annealing, without further lowering hydroxyl accessibility. Recent modelling of pore structure alongside functional groups points the same way [7, 15].

Table 1. Proposed factor structure and response set for the thermal modification programme

Variable	Type	Proposed levels or range	Role
Species	Categorical	Populus alba, Populus nigra, Salix alba	Predictor
Tissue	Categorical	sapwood, heartwood (separated)	Predictor
Reactor system	Categorical	open (N ₂ purge); closed	Predictor

Variable	Type	Proposed levels or range	Role
		(sealed, autogenous)	
Initial moisture content	Continuous	0, 8, 20 % (oven-dry, air-dry, green)	Predictor
Treatment temperature	Continuous	160, 180, 200, 220 °C	Predictor
Treatment duration	Continuous	1, 3, 5 h	Predictor
Mass loss	Continuous	gravimetric, oven-dry basis	Process integrator
Acetyl content	Continuous	saponification + HPLC, mmol g ⁻¹	Chemical response
Xylan and glucan content	Continuous	two-stage hydrolysis + HPAEC	Chemical response
Klason + acid-soluble lignin	Continuous	gravimetric + UV at 205 nm	Chemical response
β-O-4 abundance	Continuous	2D HSQC NMR on isolated lignin	Chemical response
Crystallinity index	Continuous	XRD, Segal and deconvolution	Chemical response
Volatile products	Continuous	TD-GC-MS: acetic acid, furfural, HMF	Chemical response
Accessible OH	Continuous	D ₂ O exchange in DVS, mmol g ⁻¹	Linking variable
EMC and hysteresis	Continuous	DVS, 0–95 % RH, Hailwood–Horrobin	Physical response
Anti-swelling efficiency	Continuous	radial and tangential, %	Physical response
MOR and MOE	Continuous	ISO 13061-3, ISO 13061-4	Physical response

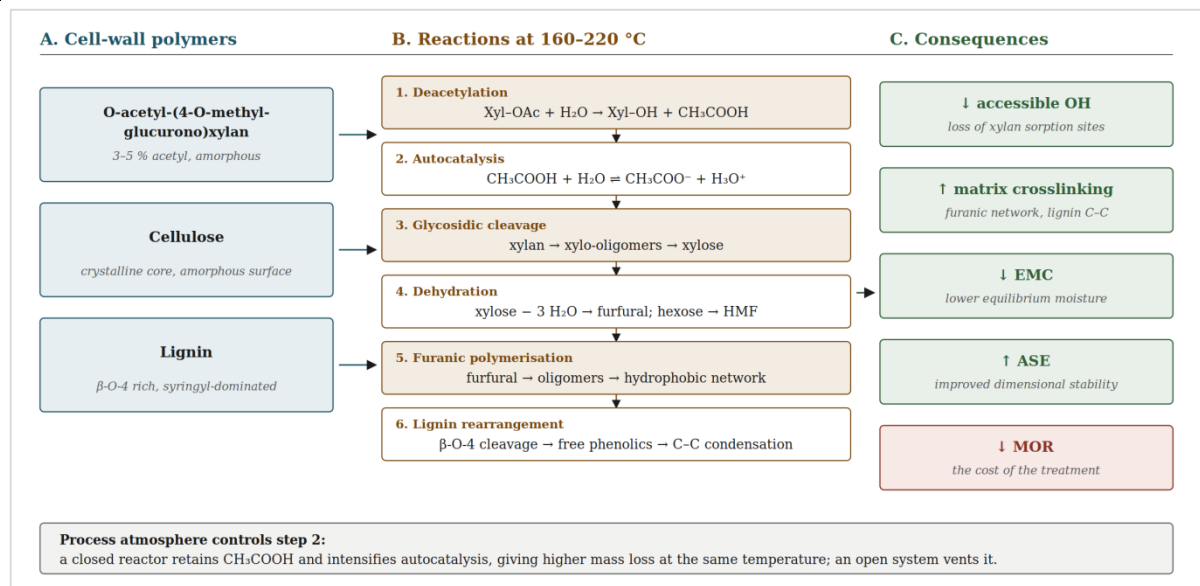


Fig. 1. Reaction network operating in the wood cell wall during thermal modification and its physical consequences

The scheme is compiled from the sources cited above and is drawn as a working hypothesis for poplar, whose acetyl content and lignin composition differ from the species on which most of the evidence was obtained.

The reaction network has an internal logic that explains why thermal modification behaves as it does, and why it is so sensitive to apparently minor process choices. Deacetylation is the trigger: it is the fastest reaction, it consumes water rather than producing volatile carbon, and it converts a chemically inert ester into a catalyst. Everything downstream depends on the fate of that acetic acid. In a sealed reactor the acid accumulates, the cell wall pH drops, glycosidic hydrolysis accelerates and mass loss at a given temperature is higher; in a vented system much of it escapes and the same nominal schedule produces a milder material [1, 26]. Two processes described by the same temperature and time can therefore differ substantially in chemistry, which is the strongest argument for reporting reaction extents rather than schedules.

The unresolved mechanistic question is what actually controls the reduced equilibrium moisture content. If accessible hydroxyl groups were the sole determinant, the correlation between hydroxyl accessibility and equilibrium moisture content would be tight, and it is not [14, 27]. The alternative account holds that heating anneals and crosslinks the amorphous matrix, so the cell wall becomes mechanically less able to accommodate water even where sorption sites remain [8], an interpretation consistent with the reduced hysteresis observed in treated material and with the furanic network identified spectroscopically [20]. These are not mutually exclusive, and the design proposed here is intended to weight them rather than to choose between them: deuterium exchange gives the site density, the sorption isotherm and its hysteresis give the matrix response, and the two enter the same correlation analysis.

The limitations should be stated. Reaction extents measured on ground material do not resolve the gradient between surface and core of an industrial board, so laboratory conclusions transfer to production only with a stated size caveat. Isolated lignin is not cell-wall lignin, and any isolation procedure alters the β -O-4 count it is meant to measure. Strength loss accompanies every useful degree of modification and cannot be engineered away, only traded against stability [11]. Finally, correlation across a designed factor set identifies which reactions travel with which properties; it does not by itself establish that one causes the other.

CONCLUSIONS

This article reframes thermal modification of fast-growing poplar as a chemical problem rather than a process-schedule problem. The reaction network is identified as a sequence in which deacetylation of glucuronoxylan generates the acid that catalyses hemicellulose hydrolysis, the resulting pentoses dehydrate to furfural and polymerise into a hydrophobic furanic network, and lignin simultaneously cleaves and recondenses. The proposed programme measures the extent of each of these steps independently, rather than collapsing them into mass loss, and correlates them with accessible hydroxyl concentration, sorption behaviour, dimensional stability and bending strength.

The practical significance for the wood-processing industry is that a chemically specified process can be transferred between reactors and species, whereas a schedule cannot. If the relative contributions of hydroxyl loss and matrix crosslinking can be weighted, treatment conditions can be selected to reach a target dimensional stability at the lowest strength penalty, which is the constraint that currently limits the use of thermally modified timber in load-bearing applications.

The planned doctoral work follows three stages. The first is to establish the compositional baseline of local *Populus alba* and *Populus nigra*, sapwood and heartwood separately, and to validate the acetyl and β -O-4 determinations on untreated material. The second is to run the open and closed treatment matrix and to build the reaction-extent dataset. The third is to measure hygroscopic and mechanical response on the same specimens and to test, against those data, whether hydroxyl accessibility or matrix crosslinking better accounts for the observed reduction in equilibrium moisture content in this species.

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