Constructive Thermochemistry: A New Framework for Sub-Destructive Carbonaceous Material Conversion

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Abstract. The thermochemical conversion of carbonaceous materials has historically operated under a destructive paradigm: the application of heat at elevated temperatures (typical range 250 to >1200 °C) to break molecular bonds and decompose complex organic structures into simpler products. This paper introduces constructive thermochemistry, a fundamentally different approach in which moderate thermal energy (in the temperature window 170 to 190 °C) is applied under vacuum (50 to 150 torr) in an oxygen-depleted environment with continuous mechanical agitation to activate polymerization, condensation, and cross-linking reactions that build molecular complexity rather than destroy it. Three primary biogenic mechanisms are identified: hemicellulose thermolysis, lignin condensation and repolymerization, and Maillard-type melanoidin formation. Each represents a chemical transformation of the natural polymeric constituents of the feedstock. A fourth mechanism, plastic-biogenic synergistic integration, is primarily physical: softened synthetic thermoplastics infiltrate and bind the chemically transformed biogenic matrix. Additional reaction pathways (cellulose surface modification, lipid cross-linking, carbohydrate caramelization, radical coupling, and others) are identified as likely contributors but await spectroscopic confirmation. Each primary mechanism is validated against independent peer-reviewed literature. Operating simultaneously on heterogeneous carbonaceous feedstock, these mechanisms produce a novel polymeric composite material exhibiting properties not predicted by any single mechanism alone. Two aspects of novelty are claimed here: first, the application of these mechanisms to heterogeneous mixed carbonaceous feedstocks, a context in which no prior thermochemical study has operated; and second, the deliberate engineering of vacuum-driven anhydrous conditions to optimize constructive reactions, a thermodynamic strategy that repurposes conditions documented in adjacent literatures (thermal wood modification, industrial polycondensation) toward an objective, namely constructive material formation from mixed carbonaceous waste, that those literatures never pursued. Dynamic Organic Repolymerization (DOR) the process through which this framework was discovered and validated over a decade of operational development, is described as the first engineered implementation of constructive thermochemistry.

1. The Thermochemical Landscape

The conversion of carbonaceous materials through the application of heat is among the oldest and most consequential technologies in human civilization. From charcoal production in antiquity to modern industrial gasification, the fundamental logic of established thermochemical processes has remained consistent: apply sufficient thermal energy to overcome the bond dissociation energies of complex organic molecules, breaking them down into simpler, more useful products. Pyrolysis (400 to 800 °C), gasification (700 to >1200 °C), torrefaction (200 to >300 °C), and hydrothermal carbonization (180 to 260 °C under pressure with liquid water) all operate on this principle, varying primarily in temperature, atmosphere, and the presence or absence of water and oxygen.

These processes are well characterized, commercially deployed, and constitute the established thermochemical paradigm. What they share, despite their diversity, is a common thermodynamic orientation: the deliberate application of energy sufficient to break the covalent bonds that hold organic macromolecules together. The products, whether syngas, bio-oil, biochar, or torrefied biomass, are the fragments and rearrangements that result from controlled decomposition.

This paper proposes that the thermochemical landscape contains a regime that has not been systematically investigated: the narrow temperature window below the destructive threshold in which thermal energy is sufficient to activate polymerization, condensation, and cross-linking reactions but insufficient to initiate the bond-breaking, charring, and decomposition that characterize the established paradigm. In this regime, heat does not destroy molecular complexity, but rather builds it. We term this ‘constructive thermochemistry’ and present it as a new framework for the thermochemical conversion of carbonaceous materials.

2. Surface Carbon as Polymeric Substrate

The carbonaceous materials available at the Earth’s surface, from biomass and agricultural residues to forestry waste, food waste, textiles, natural rubber, and the organic fraction of municipal solid waste, are fundamentally polymeric in nature. They are composed of natural macromolecules: cellulose, hemicellulose, lignin, proteins, lipids, and their derivatives. In the case of mixed waste streams, synthetic polymers (polyethylene, polypropylene, polystyrene, and others) are also present. This polymeric character is the defining chemical feature of surface carbon, distinguishing it from subsurface carbon (petroleum, coal, natural gas) which has undergone geological transformation over millions of years, losing much of its original polymeric architecture through diagenesis and catagenesis.

Humanity has long recognized that surface carbon polymers are useful substrates for material creation through chemical synthesis, biochemical conversion, and mechanical processing. Polylactic acid (PLA) is produced from corn starch through fermentation and polycondensation. Cellulose acetate is synthesized from wood pulp through esterification. Vulcanized rubber is created by cross-linking natural polyisoprene with sulfur. Cotton, a nearly pure cellulose polymer, is spun and woven into textiles. In each case, the polymeric character of the feedstock is preserved and enhanced, not destroyed, to create a useful material. These are constructive processes.

Yet the thermochemical processing of surface carbon has historically treated polymeric structure as an obstacle to be overcome rather than a resource to be harnessed. Pyrolysis and gasification break these polymers apart. Torrefaction partially degrades them (as does thermal wood modification, operating at the lower temperature range of torrefaction). Hydrothermal carbonization relies on hydrolysis, the water-mediated cleavage of polymer bonds, as a primary reaction mechanism. The thermochemical paradigm has been, almost exclusively, a destructive one.

Constructive thermochemistry begins from a different premise: that the polymeric nature of surface carbon can be exploited thermochemically, not just through chemical synthesis, biochemical conversion, or mechanical processing, to create new materials. If thermal energy can be applied in a regime that activates condensation and cross-linking reactions without initiating destructive decomposition, the natural polymeric architecture of the feedstock can be reorganized and enhanced rather than dismantled. The result is not a degradation product but a new polymeric composite of greater molecular complexity, mechanical integrity, and thermodynamic stability than the original feedstock. This represents the central contribution of this work: the identification and characterization of a previously uninvestigated regime within thermochemistry, and the demonstration that constructive outcomes are achievable through thermal processing alone. It also carries the most consequential practical implication: a thermochemical pathway for the constructive conversion of surface carbon into engineered materials, a capability that has until now existed only in chemical, biochemical, and mechanical processing.

3. The Discovery Pathway

The identification of the constructive thermochemical regime did not emerge from theoretical prediction. It arose from a cross-disciplinary insight, followed by systematic empirical investigation conducted by this author, whose career had been spent inside the very systems that this discovery would ultimately reframe.

The author developed and directed synthetic fuels, bioenergy, and pyrolysis/gasification programs over the years preceding this work. This background provided insights into pyrolysis and gasification vessels: the behavior of heterogeneous organic materials at elevated temperatures, the engineering challenges of uneven heat distribution, the failure modes that arise when complex feedstocks encounter temperature gradients sufficient to initiate charring in some regions while leaving others unprocessed, and the incomplete conversion that results when the pathway from ambient to high temperatures is not carefully managed. It was this understanding of the destructive regime, acquired through years of hands-on operational experience, that some years later motivated the investigation of what might occur below it. The ideas that led to constructive thermochemistry thus were inspired by the realization that the sub-destructive regime remained unexplored simply because it was overlooked, and processes aimed merely at materials drying operated at lower temperatures (e.g. <160 °C) and involved very different process considerations.

The initial insight was deceptively simple but proved foundational. The author realized that what is commonly called “waste” as if it is a substance, and even treated as such throughout technical literature, is indeed merely a definitional construct. It is a collection of materials, each with its own polymer chemistry, thermal behavior, and degradation profile. A municipal solid waste stream, having had its inorganic fractions removed, is in chemical terms mostly an assemblage of cellulose, hemicellulose, lignin, proteins, lipids, and bio- or synthetic thermoplastics in varying proportions. To understand what thermal energy does to this assemblage, one must first understand what it does to each constituent individually, and then determine whether conditions exist under which their individual thermal responses could combine to produce something constructive rather than destructive. This realization reframed the problem entirely: rather than treating a feedstock as a bulk material to be processed at a given temperature, the author recognized that the thermal behavior of each polymeric component needed to be understood on its own terms before the system-level behavior could be predicted or engineered.

The author’s materials research commenced in 2014 with a systematic investigation across multiple disciplines. The plant science literature documented hemicellulose thermal behavior at onset temperatures far below those used in conventional thermochemical processing. The lignin chemistry literature characterized condensation and repolymerization reactions that the biorefining field had been trying to suppress for decades. The food science literature contained extensive characterization of Maillard-type browning between reducing sugars and amino compounds under thermal conditions. The polymer engineering literature described thermoplastic behavior at melt temperatures and the principles governing polymer-matrix composite formation. No single discipline had considered the simultaneous activation of all these reaction classes in a mixed feedstock. The cross-disciplinary synthesis was the key.

By 2015, this research had generated specific, testable hypotheses about what should happen to a heterogeneous carbonaceous feedstock under carefully controlled conditions. The hypotheses required a particular combination of temperature, pressure, atmosphere, agitation, and dwell time, each parameter serving a specific thermodynamic function: temperature sufficient to activate the identified constructive reactions but insufficient to cross the destructive threshold; vacuum to depress the boiling point of water and continuously extract both pre-existing moisture and the water produced by condensation reactions, shifting equilibrium toward polymer formation; a sealed atmosphere to exclude oxygen; and mechanical agitation to ensure both thermal uniformity and the intimate contact between constituents that cross-linking requires. A series of experiments tested these hypotheses, systematically varying conditions across the sub-destructive regime.

What emerged from these experiments was a material unlike anything in the thermochemical conversion literature. The author observed that the output was not a compacted mass of identifiable waste particles. It was a homogeneous, dark, remarkably uniform polymeric substance. While still warm from the vessel, it had the consistency of a viscous putty: thick, moldable, cohesive, and without any visible distinction between what had been paper, food waste, yard debris, or plastic. It could be shaped by hand. As it cooled, it hardened into a dense, mechanically coherent solid. Those who had worked with conventional refuse-derived densified products recognized immediately that this was something categorically different. The original feedstock components were no longer distinguishable. The material had not merely been dried and compressed, but instead had been fundamentally transformed.

The selective depolymerization that had been predicted was occurring, but it was accompanied by something the author had not anticipated at this magnitude: repolymerization. The fragments released by selective bond cleavage were recombining into new polymeric structures under the specific combination of temperature, vacuum, and mechanical action in the sealed vessel. This was not incremental improvement of a feedstock preparation process. It was the creation of a genuinely new material from unsorted mixed carbonaceous feedstock, at temperatures the entire field had considered too low to accomplish anything meaningful.

The author has designated the process Dynamic Organic Repolymerization (DOR) and the resulting material EGS-6. A comprehensive patent portfolio was filed beginning in late 2015, covering process methods, vessel design, agitation systems, and product compositions, later extended to engineered composites, polymer powders, and additive manufacturing applications as the author's research and development investigation program continued [1]. Over the subsequent decade, the process has been validated through continuous operational development and through independent analytical characterization of the product across multiple feedstock compositions and production campaigns. More than 100 patents have been issued in the United States and worldwide. The patent portfolio covers specific process implementations, apparatus designs, and material compositions. The theoretical framework presented in this paper, the identification and characterization of constructive thermochemistry as a distinct thermochemical regime, represents a separate and independent scientific contribution.

[1] See, e.g., U.S. Patent Nos. 9,771,536 (solid fuel composition, 2017); 10,738,255 (process, 2020); 11,124,725 (process vessel, 2021); 11,254,888 (solid fuel composition, 2022); 11,541,362 (agitator rotors and agitator systems for solids, 2023); 11,692,082 (compositions containing solid waste material, 2023); 11,781,083 (process vessel, 2023); 11,879,106 (process for forming solid fuel composition from mixed solid waste, 2024); 11,964,314 (powders comprising solid waste materials, 2024); and additional filings.

4. The Constructive Thermochemical Window

Constructive thermochemistry operates within a specific set of thermodynamic conditions, each serving a defined chemical function. These conditions are not arbitrary process parameters; they are the engineered environment required for constructive reactions to proceed while destructive reactions remain thermodynamically or kinetically inaccessible. The detailed engineering by which these conditions are achieved in the DOR process vessel is beyond the scope of this framework paper and will be addressed in subsequent publications; the present discussion focuses on the thermodynamic rationale for each condition.

4.1 Temperature: 170 to 190 °C

The lower bound of the constructive window (approximately 170 °C) corresponds to the onset temperatures of the primary constructive reactions. Ironically (given that these experiments would result in the discovery of a *constructive* thermochemistry regime), the author first chose to use this benchmark to investigate whether partial hemicellulose thermal degradation would result in an engineered fuel with superior combustion characteristics (without having to use higher torrefaction temperatures, which create a number of operational and sometimes regulatory challenges due to devolatilization). Hemicellulose thermal degradation initiates at approximately 170 to 180 °C, as documented across multiple independent thermogravimetric and compositional studies of lignocellulosic biomass. Apaydin Varol and Mutlu (2023), using thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy (TGA-FTIR) analysis of biomass components, measured the onset of xylose (hemicellulose model compound) thermal decomposition at 173 °C, with cellulose remaining stable until 291 °C, and lignin initiating decomposition at 170 °C. Lv et al. (2010) found hemicellulose degradation principally in the 180 to 340 °C range with a shoulder peak at approximately 205 °C. Werner et al. (2014) demonstrated that xylan, the dominant hemicellulose in hardwood and paper pulp, was consistently the least thermally stable of seven hemicelluloses studied, attributing this to the inherently lower stability of 1,4-glycosidic bonds in anhydroxylopyranose compared to the 1,6-glycosidic bonds in cellulose. Winandy and Krzysik (2007), in a USDA Forest Products Laboratory study of medium-density fiberboard (MDF) composites, found that arabinan and galactan (hemicellulose side chains) were dramatically reduced at 180 °C, with discernible changes in mechanical properties appearing at mat core temperatures near 175 °C. The glass transition temperature of lignin, the point at which the amorphous aromatic polymer becomes mobile and chemically reactive, ranges from approximately 130 to 190 °C depending on moisture content and botanical origin. Polyethylene softens at 110 to 130 °C and polypropylene at 130 to 170 °C, ensuring both common synthetic polymers are in a flowable state within the constructive window.

Maillard-type reactions between reducing sugars and amino compounds have been documented in food waste systems at temperatures as low as 132 °C. However, the Maillard products formed below approximately 170 °C are relatively trivial from a materials science perspective: low-molecular-weight intermediates and early-stage Amadori compounds that do not contribute meaningfully to product structure, mechanical properties, or chemical stability. The formation of high-molecular-weight, recalcitrant, hydrophobic polymeric melanoidins, which meaningfully impact properties, inhibit anaerobic processes, and reduce biodegradability, becomes more pronounced and consequential during thermal pretreatment at temperatures above 160 °C and, especially, above 175 °C (Li, Y. et al., 2024; Yang, M. et al., 2023). This threshold represents a meaningful activation point not merely for the Maillard reaction itself, but for the production of melanoidin polymers whose material properties matter for constructive thermochemistry. It is one of several reasons that the constructive window begins at 170 °C rather than at lower temperatures where some individual reactions may technically initiate.

The upper bound (approximately 190 °C) is defined by the onset of reactions that transition from constructive to destructive character. Ring fusion in lignin char, the earliest stage of aromatic polycondensation, initiates at approximately 200 °C (Zhang et al., 2020). Lignin thermolysis becomes significant starting at approximately 175 °C (with initial modification noted at ~150 °C due to loss of labile structures) and significant polymerization also takes place at ~175 °C or above (Chua et al., 2019).

Heterolytic cleavage of phenolic α-ether bonds in lignin model compounds, which produces highly reactive quinone methide intermediates that can lead to further depolymerization or condensation reactions, begins at approximately 200 °C (Kawamoto, 2017). Cerc Korošec et al. (2024), modifying oak wood at temperatures from 170 to 210 °C, measured mass losses of 1.28% at 170 °C, 1.82% at 180 °C, and 2.82% at 190 °C, rising sharply to 4.65% at 200 °C and 7.53% at 210 °C, an acceleration indicating the transition from selective modification to bulk degradation. Above approximately 200 °C, the chemistry shifts progressively from building molecular complexity to dismantling it. The 170 to 190 °C window is therefore not an arbitrary operating range but a thermodynamically defined regime: the temperatures at which constructive reactions are kinetically accessible while destructive reactions are not.

This window requires careful and uniform heat delivery. Unlike higher-temperature processes where rapid heating and steep thermal gradients are tolerable, constructive thermochemistry demands that every particle in the feedstock reaches the target temperature without any region exceeding the destructive threshold. Slow, conductive heating through the vessel wall and heated agitator elements, combined with continuous mechanical mixing, achieves the thermal homogeneity this requires. Batch residence times in the reaction vessel are typically 60 to 90 minutes, sufficient for the constructive reactions to reach substantial completion as evidenced by product properties. Winandy and Krzysik (2007) introduced the concept of cumulative thermal load (degree-seconds above a threshold temperature), demonstrating that the extent of chemical modification in wood is a function of both temperature and time rather than temperature alone, a principle that explains why the DOR process achieves substantial transformation at temperatures the field had considered too low for meaningful chemistry. This is a fundamental departure from conventional thermochemical processing, where temperature non-uniformity is an accepted engineering trade-off.

4.2 Vacuum: 50 to 150 torr

The role of vacuum in constructive thermochemistry extends well beyond drying. At operating pressures of 50 to 150 torr (6.7 to 20 kPa), the boiling point of water drops to approximately 38 °C at 50 torr, 52 °C at 100 torr, and 60 °C at 150 torr. Even at the upper end of the operating range, water boils more than 110 °C below the temperature at which constructive reactions initiate. Free water flashes to vapor almost immediately upon the application of modest heat, and physically bound water is progressively desorbed well before the feedstock reaches the constructive window.

This early and thorough water removal is a thermodynamic prerequisite for the constructive chemistry. The presence of liquid water in the reaction environment promotes hydrolysis, the water-mediated cleavage of polymer bonds, which competes directly with the condensation reactions that constructive thermochemistry seeks to activate. The thermal wood modification literature provides direct peer-reviewed support for this thermodynamic logic. Hill, Altgen, and Rautkari (2021), in a comprehensive review published in *Journal of Materials Science*, categorized thermal modification processes into wet (superheated steam, saturated steam, liquid water) and dry (air, inert atmosphere, vacuum) classes and explicitly concluded that dry process conditions are more favorable for the formation of cross-linking reactions, because anhydrous conditions favor the formation of furfural derivatives from the polysaccharide content, and these degradation products are able to participate in reactions with the lignin and remaining polysaccharide content, creating insoluble hydrophobic materials. In wet processes, by contrast, water increases polymer mobility and hydronium ions catalyze glycosidic bond hydrolysis, a competitive pathway that degrades rather than builds polymeric structure. The DOR vacuum environment achieves a more thorough version of the dry conditions that this wood science literature identifies as constructive: not merely the absence of added water, but the active, continuous removal of both pre-existing moisture and the water generated by the constructive reactions themselves.

The vacuum serves a second essential function: it continuously extracts the water produced by condensation reactions themselves. Lignin condensation, Maillard browning, and hemicellulose dehydration all release water as a byproduct of new bond formation. By Le Chatelier's principle, the continuous removal of this reaction product shifts equilibrium toward further condensation, creating a thermodynamic feedback loop: condensation produces water, vacuum removes water, equilibrium shifts further toward condensation. This is the same mechanism by which industrial polycondensation produces high-molecular-weight polymers such as nylon and polyesters. PLA prepolymer reactors, for example, operate at approximately 170 °C under vacuum specifically to drive condensation polymerization forward by removing water. The DOR process applies this well-established industrial principle to the constructive thermochemistry of heterogeneous carbonaceous feedstocks.

Third, the vacuum maintains a severely oxygen-depleted atmosphere. Upon initial evacuation to 50 to 150 torr, residual oxygen partial pressure is reduced proportionally from ambient levels.

However, as the feedstock heats and water vapor, acetic acid, furfural, and other volatiles evolve from the constructive reactions, these evolved gases progressively displace residual air in the headspace. Within minutes of reaching operating temperature, the vessel atmosphere is dominated by water vapor and light organic volatiles rather than residual air, driving the effective oxygen partial pressure to negligible levels. This prevents the oxidative reactions that would degrade reactive intermediates and polymeric products, without requiring continuous purge of inert gas.

The 50 to 150 torr range provides operational flexibility while maintaining all three thermodynamic functions. During initial heating, deeper vacuum maximizes the rate of moisture removal. As temperatures rise and volatile organic compounds evolve from hemicellulose thermolysis and Maillard reactions, system pressure may increase toward the upper end of the range. The equilibrium driving force, the oxygen exclusion, and the prevention of liquid water all remain effective throughout.

4.3 Sealed Atmosphere, Mechanical Agitation, and Process Sequencing

The reaction vessel is sealed against atmospheric ingress while connected to a continuous vacuum extraction system with condensation capability. This configuration, standard in industrial vacuum reactor design, maintains the sub-atmospheric environment throughout the reaction while continuously removing evolved water vapor and volatiles through a condenser. The distinction is important: the vessel is sealed against oxygen and atmospheric moisture, not hermetically closed. The vacuum pump operates continuously, extracting vapors and maintaining the target pressure range.

Continuous mechanical agitation serves multiple critical functions. It ensures thermal homogeneity by preventing localized hot spots that could exceed the destructive threshold. It promotes intimate physical contact between the heterogeneous feedstock components, a prerequisite for cross-linking and synergistic integration. And it facilitates the release and extraction of volatiles and water vapor from the particle bed, maintaining the dry conditions essential for condensation chemistry.

A critical operational insight, identified by the author during DOR development, concerns the sequencing of biogenic transformation and plastic encapsulation. Within the constructive window, thermoplastic polymers (PE, PP) soften and become flowable. If allowed to melt and consolidate prematurely, these softened plastics would encapsulate the biogenic particles, shielding them from further thermal exposure and effectively halting the constructive chemistry of the biogenic fraction. The author recognized this risk and engineered the agitation regime to prevent it: continuous mechanical action maintains the feedstock in a distributed, non-compacted, flowing state throughout the vessel residence time, ensuring that all biogenic particles receive sustained thermal exposure and undergo the full sequence of constructive reactions (hemicellulose thermolysis, lignin condensation, Maillard chemistry) before any consolidation with the softened plastic phase occurs. The development of a specialized heated agitator rotor system, co-invented with an engineering colleague in the aerospace industry and protected by issued patent (U.S. Patent No. 11,541,362), was essential to achieving this process sequencing. Consolidation into the final composite morphology, in which the now-chemically-transformed biogenic matrix integrates with the softened synthetic polymer phase, occurs during subsequent discharge and densification, not during the vessel reaction itself. This deliberate sequencing is what distinguishes the DOR product from a conventional wood-plastic composite: the biogenic fraction has been chemically reconstructed before it is physically bound.

The combination of these conditions, moderate temperature, vacuum, sealed-but-extracted atmosphere, continuous agitation with controlled process sequencing, creates a thermodynamic environment with no direct analog in the established thermochemical literature. It is too cool for pyrolysis or gasification, too dry for hydrothermal carbonization, and distinct from torrefaction in both its temperature range and its sub-atmospheric pressure. It is the constructive thermochemical window.

5. The Four Primary Mechanisms

Three biogenic reaction mechanisms and one primarily physical integration mechanism have been identified as the primary drivers of constructive thermochemistry within the 170 to 190 °C window. The biogenic mechanisms (hemicellulose thermolysis, lignin condensation and repolymerization, and Maillard-type melanoidin formation) are chemical transformations of the natural polymeric constituents of the feedstock. The fourth mechanism, plastic-biogenic synergistic integration, is predominantly physical: the infiltration and binding of the chemically transformed biogenic matrix by softened synthetic thermoplastics. Each mechanism is independently documented in the peer-reviewed literature. Their simultaneous activation in a heterogeneous carbonaceous feedstock under the conditions described in Section 4 constitutes the novel contribution of this work. Additional reaction pathways (cellulose surface modification, lipid cross-linking, carbohydrate caramelization, radical-mediated coupling, and possible transesterification) are likely contributors to the final product character but are discussed in Section 9 as priorities for spectroscopic confirmation.

For each mechanism, the original observation within the author's core DOR development program (2014 to 2015) is presented alongside independent literature that has since corroborated the underlying science.

5.1 Hemicellulose Thermolysis

Hemicellulose, the most thermally labile component of lignocellulosic biomass, undergoes selective thermal degradation beginning at approximately 170 to 180 °C. Unlike cellulose (stable until approximately 290 °C) or lignin (which degrades across a broad range), hemicellulose decomposition initiates at temperatures accessible within the constructive window. The primary reactions involve cleavage of glycosidic bonds and dehydration of sugar units, releasing acetic acid, furfural, and water of constitution.

In the DOR process, this selective thermolysis was identified as a critical enabling reaction: it releases volatile fragments and water while preserving the more stable cellulose and allowing lignin structures to go through selective thermolysis as well as polymerization. The energy previously stored in labile hemicellulose bonds is redistributed, with mass decreasing while energy content per unit mass increases, a phenomenon termed energy densification. The released organic acids, particularly acetic acid from acetyl groups, may also serve as mild catalysts for subsequent condensation reactions.

The convergence of independent evidence for hemicellulose onset temperatures in the 170 to 180 °C range is striking. Thermogravimetric studies of isolated biomass components (Lv et al., 2010; Apaydin Varol & Mutlu, 2023), differential analysis of seven hemicellulose species (Werner et al., 2014), USDA laboratory studies of wood fiber composites (Winandy & Krzysik, 2007), and a comprehensive review of the thermal wood modification literature (Hill et al., 2021) all place the onset of meaningful hemicellulose degradation in this same narrow range. Most recently, Salami and Klinghoffer (2026), in a torrefaction study of actual MSW fractions (paper cups, white spruce sawdust, forest residues, wheat straw, and lemon peels) under N_2 and CO_2 atmospheres, identified a derivative thermogravimetric (DTG) peak in the 160 to 200 °C range for all fractions tested, which they attributed specifically to the onset of hemicellulose decomposition. This is, to the author’s knowledge, the only study in the literature to document hemicellulose thermolysis in actual MSW fraction materials rather than isolated model compounds, and it independently corroborates the author’s original constituent-level insight: the biogenic components of municipal waste undergo thermolysis in the constructive temperature window. This study, published more than a decade after the author's original operational development and patent filings, provides independent analytical confirmation of the constituent-level thermal behavior that the DOR process was engineered to exploit.

Hill et al. (2021) further documented that under dry thermal modification conditions, furfural derivatives released from hemicellulose degradation participate in reactions with the lignin and remaining polysaccharide content rather than being leached away as occurs under wet (steam) conditions. This finding is directly relevant to the DOR environment, where vacuum ensures thoroughly dry conditions and the furfural released by hemicellulose thermolysis remains available to contribute to constructive cross-linking rather than being lost to hydrolysis. The thermal modification of wood literature more broadly documents substantial hemicellulose degradation at treatment temperatures of 160 to 220 °C, with resulting improvements in dimensional stability and biological resistance attributed to the removal of this hygroscopic component and the formation of new hydrophobic condensation products (Hill et al., 2021; Windeisen & Wegener, 2008).

5.2 Lignin Condensation and Repolymerization

Lignin, the aromatic, amorphous, three-dimensional polymer that provides structural rigidity to plant cell walls, undergoes condensation and repolymerization reactions when heated above its glass transition temperature, preferentially under anhydrous conditions. These reactions are consistent with the formation of new carbon-carbon bonds between aromatic fragments, creating larger, more complex, and more recalcitrant molecular structures.

This mechanism was hypothesized during DOR development based on observed material properties: mechanical rigidity, darkening, resistance to solvent extraction, and hydrophobicity, all consistent with increased aromatic cross-linking (patent filings, 2015). The hypothesis drew on the plant science and wood chemistry literatures, which had documented lignin condensation during thermal treatment as an unwanted side effect of pulping and biorefining.

Subsequent peer-reviewed literature has extensively characterized this mechanism. Kim and Kim (2018), reviewing lignin chemistry in *Frontiers in Energy Research*, cataloged four distinct lignin condensation pathways: radical coupling, vinyl condensation, reactive fragment polymerization, and reactive functional group-induced repolymerization. Gong and Shuai (2023) titled their review "Lignin condensation: an unsolved mystery," highlighting that lignin repolymerization remains one of the least understood phenomena in biomass chemistry. Funaoka et al. (1990) confirmed that significant lignin condensation occurs in wood heated to temperatures approaching 220 °C. Brandner et al. (2025), studying lignin behavior in flow-through reactors, documented significant condensation as a function of temperature and residence time, further confirming that condensation is a dominant lignin response to thermal treatment in the relevant temperature range.

Hill et al. (2021) provide additional support, documenting that thermal modification produces an increase in Klason lignin content attributable to condensation reactions between lignin and polysaccharide breakdown products, with increased condensed C–C linkages. Critically, they found that these condensation reactions are more favorable under dry process conditions (precisely the vacuum-driven anhydrous environment of the DOR process) whereas wet conditions promote competing hydrolysis pathways that fragment rather than build the lignin network.

Lignin condensation can occur across a range of moisture conditions; Funaoka et al. (1990) documented diphenylmethane-type structures forming in both wet and dry wood approaching 220 °C. The relevant distinction is not that water prevents condensation, but that anhydrous conditions shift the competitive balance away from hydrolysis and toward net condensation and cross-linking.

The critical insight for constructive thermochemistry is that the biorefining field has treated lignin condensation as a problem to be solved, an "undesirable reaction" (Kim & Kim, 2018) that limits the yield of monomeric products. In constructive thermochemistry, lignin condensation is the mechanism by which a new polymeric material is built. The observed product properties are consistent with the formation of new C–C bonds between aromatic fragments, the chemistry needed to create a mechanically durable, chemically stable, hydrophobic composite from heterogeneous carbonaceous feedstock. Direct spectroscopic confirmation of specific bond types in DOR-derived materials is the subject of ongoing investigation and represents a priority for collaborative research.

5.3 Maillard Reaction and Melanoidin Formation

The Maillard reaction, the non-enzymatic condensation of reducing sugars with amino compounds, is one of the most extensively studied reactions in food chemistry. First described by Louis-Camille Maillard in 1912, it produces a complex family of high-molecular-weight polymeric compounds known as melanoidins.

The role of Maillard-type chemistry in DOR was hypothesized based on three converging observations: the mixed feedstock contains abundant reducing sugars (from hemicellulose degradation and food waste) alongside amino compounds (from protein-containing food waste and textiles); the processing conditions (above 170 °C, extended dwell time, low water activity under vacuum) are precisely those known to promote advanced-stage Maillard browning; and the product exhibits the characteristic dark coloration, recalcitrant character, and polymeric homogeneity associated with high-molecular-weight melanoidin formation (patent filings, 2015).

Recent literature has confirmed that Maillard reactions produce consequential polymeric products during thermal pretreatment of organic solid waste. For instance, the formation of high-molecular-weight, recalcitrant, hydrophobic polymeric melanoidins, which meaningfully impact properties, inhibit anaerobic processes, and reduce biodegradability, becomes more pronounced and consequential during thermal pretreatment at temperatures above 160 °C and, especially, above 175 °C (Li, Y. et al., 2024; Yang, M. et al., 2023). The properties attributed to melanoidins in this literature, recalcitrant, biorefractory, dark-colored, hydrophobic, correspond to properties observed in DOR-derived materials.

The wastewater (sludge) and food waste treatment literature has uniformly characterized Maillard reactions during thermal processing as an unwanted side effect that reduces anaerobic digestibility, inhibits microbial activity, and creates compounds that interfere with biogas production. Constructive thermochemistry inverts this framing. The melanoidins that are problematic for biological treatment are precisely the recalcitrant, stable polymers desired in a constructive material. To the author's knowledge, this represents the first context in which Maillard-type reactions in waste processing are deliberately harnessed rather than suppressed.

The progressive release of chemically bound water during hemicellulose thermolysis creates transient intermediate water activity conditions favorable to advanced Maillard kinetics, even as the vacuum system continuously removes this water to prevent competing hydrolysis.

5.4 Plastic-Biogenic Synergistic Integration

Mixed carbonaceous waste streams often contain significant quantities of synthetic thermoplastic polymers, predominantly polyethylene (softening at approximately 110 to 130 °C) and polypropylene (softening at approximately 130 to 170 °C). Within the constructive thermochemical window, these polymers are fully softened and in a flowable, viscous state.

The behavior of these softened thermoplastics during DOR processing is primarily physical rather than chemical. At approximately 180 °C, polyolefins do not readily form new covalent bonds with biomass constituents; they soften, flow, and infiltrate the surrounding matrix. The key observation during DOR development was that under continuous mechanical agitation, these softened synthetic polymers infiltrate the porous structure of the simultaneously reacting biogenic material, forming a continuous hydrophobic matrix that encapsulates and binds the lignocellulosic and melanoidin components. As described in Section 4.3, the agitation regime is specifically engineered to ensure that this infiltration and binding occurs after the biogenic fraction has undergone its chemical transformation, not before.

The result is not a simple mixture but an integrated composite in which the synthetic polymer phase provides hydrophobic, mechanically binding continuity and the chemically transformed biogenic phase provides structural bulk and the cross-linked architecture created by the constructive reactions. This synergistic integration explains several otherwise puzzling properties of the product: its hydrophobicity exceeds what the biogenic content alone would produce, its mechanical durability exceeds what either phase would exhibit independently, and its homogeneous appearance reflects complete integration of originally discrete feedstock components. The synthetic polymer phase seals the biogenic matrix against moisture re-uptake and biological attack, while the biogenic phase provides the structural framework that prevents the synthetic polymer from behaving as an amorphous melt.

This combination of a chemically transformed biogenic matrix with physical thermoplastic binding distinguishes the DOR product from conventional wood-plastic composites (WPCs), in which untreated wood flour is mechanically blended with molten plastic. In DOR, the biogenic phase has undergone constructive thermochemical transformation before integration with the plastic phase. The resulting material properties, discussed in Section 7, reflect this distinction.

6. Synergistic Interaction

The four mechanisms described in Section 5 do not operate independently. Their simultaneous activation on a heterogeneous feedstock under the conditions described in Section 4 produces outcomes that no single mechanism alone would predict.

Hemicellulose thermolysis releases reducing sugars and organic acids into the reaction environment. These sugars become substrates for Maillard-type reactions with amino compounds present in the feedstock, producing melanoidin polymers. The organic acids may catalyze lignin condensation reactions, accelerating C–C bond formation. Lignin, mobilized above its glass transition temperature, undergoes repolymerization while simultaneously interacting with melanoidin products and hemicellulose degradation fragments. Following completion of these biogenic transformations, softened synthetic polymers infiltrate and bind the chemically reconstructed biogenic matrix, creating a composite that consolidates the products of all four mechanisms.

The vacuum continuously removes water, both the pre-existing moisture driven off by the depressed boiling point and the water of condensation produced by the reactions themselves, driving all equilibrium-limited condensation reactions forward. The sealed atmosphere prevents oxidative degradation. Continuous agitation ensures intimate contact between all constituents while maintaining the process sequencing described in Section 4.3.

Critically, the three biogenic chemical mechanisms operate independently of synthetic polymer presence. The DOR framework predicts that processing on purely biogenic feedstocks (lignocellulosic material with no synthetic plastic content) under the same conditions would produce the same darkened, cohesive, transformed material. In the DOR temperature range, cohesion without synthetic plastics is achieved via lignin softening and flow and furfural-derived cross-links from hemicellulose, especially under anhydrous conditions like vacuum that favor polymerization over hydrolysis. The agitation enhances particle contact for binding, yielding self-bound cohesive panels or masses. Hemicellulose thermolysis, lignin condensation, and Maillard-type melanoidin formation proceed under the vacuum-driven anhydrous conditions regardless of whether synthetic polymers are present in the feedstock. This observation strongly supports the conclusion that the constructive chemistry is not dependent on thermoplastic binding. The plastic-biogenic synergistic integration described in Section 5.4 is an additional, primarily physical mechanism that enhances the final composite properties when synthetic polymers are present, but the fundamental constructive transformations are biogenic in origin.

The product of this synergistic system is a material that none of the individual mechanisms could produce alone: a homogeneous, hydrophobic, mechanically durable polymeric composite derived from heterogeneous carbonaceous feedstock, with favorable density characteristics and remarkable resistance to biological degradation even when subjected to untreated outdoor elements for extended periods of time.

7. Empirical Evidence

The DOR process has been operationally validated over a decade of development, with product properties independently confirmed by certified analytical laboratories. The following material properties are presented as empirical evidence that the constructive reactions described above have occurred.

Material character. When discharged from the vessel at process temperature, the product exhibits a viscous, putty-like consistency: warm, moldable, cohesive, and uniform in color and texture. As it cools, it hardens into a dense, mechanically coherent solid. This thermoplastic-like behavior at temperature, followed by hardening on cooling, is consistent with a material in which softened synthetic polymers form a continuous binding matrix throughout a chemically transformed biogenic structure.

Homogeneity. Individual feedstock components (paper, cardboard, food waste, yard waste, textiles, plastics) are no longer visually or mechanically distinguishable. This is evidence of extensive integration between the biogenic and synthetic phases, a property that simple mixing, drying, or compression would not produce.

Color transformation. The product is uniformly dark brown to black, consistent with the formation of melanoidin polymers (Maillard browning) and oxidized lignin decomposition products such as quinones (Hill et al., 2021; Cerc Korošec et al., 2024). This darkening is a chemical marker, not merely a drying artifact; it correlates with the degree of thermal modification in the wood science literature and is indicative of the constructive reactions having occurred.

Moisture content. Very low moisture. In testing as an engineered fuel, it showed consistently below 2%, frequently below 1%, as measured by standard proximate analysis (ASTM D3173). This is direct evidence of the effectiveness of vacuum-driven moisture removal and the continuous extraction of condensation water.

Hydrophobicity. The product resists moisture re-uptake when exposed to ambient conditions and brief water contact, consistent with the formation of a continuous synthetic polymer matrix and hydrophobic condensed lignin and melanoidin structures.

Mechanical integrity. The product exhibits structural properties consistent with an engineered polymeric composite. It can be planed (power), cut with standard woodworking tools (power circular saw blades), accepts wood screws driven by power tools, and has been fabricated into load-bearing furniture and building structures. Material stored outdoors and untreated through northern U.S. winters (exposed to repeated freeze-thaw cycles, snow, and ice) shows no observable degradation, in contrast to conventional dimensional lumber subjected to the same outdoor exposure at the same site. These properties are consistent with the proposed mechanistic framework: the covalently cross-linked biogenic matrix (lignin condensation, melanoidin polymerization) provides structural rigidity, while the continuous thermoplastic phase provides hydrophobic protection and impact resistance.

Biological stability. The product resists microbial degradation under ambient and outdoor storage conditions (including direct exposure to the elements, on an untreated basis), consistent with the recalcitrant character of condensed lignin and melanoidin structures, combined with the hydrophobic polymer matrix that limits moisture and microbial access.

Volatile matter retention. The product retains 75 to 90% volatile matter, substantially higher than torrefied biomass or charcoal. This is a direct consequence of operating below the destructive threshold: the constructive reactions build molecular complexity without driving off the volatile organic content that higher-temperature processes release.

Conceptual mass balance. Input feedstock mass is distributed among three output streams: the solid polymeric product (the primary output), condensate (water and light organics recovered by the vacuum extraction and condensation system), and non-condensable gases (primarily CO_2 from decarboxylation and light volatiles). Typical mass retention in the solid product is broadly 70 to >85% of the input mass, often exceeding 80% depending on feedstock moisture and composition, substantially higher than torrefaction (60 to 80%) and far higher than pyrolysis (20 to 35%) or gasification (<5% solid residue). This relatively high solid yield is consistent with the constructive paradigm: reactions that build molecular complexity inherently retain more mass in the solid phase than reactions that decompose organic structures into gases and liquids. A detailed quantitative mass balance, including differentiation between water of constitution driven off by vacuum and water of condensation produced by the reactions themselves, is identified in Section 9 as a priority for systematic characterization.

These properties have been confirmed across multiple production campaigns over many years, with varying feedstock compositions. Independent analytical data from Hazen Research, Inc. (Golden, Colorado), a certified analytical laboratory, spanning the period 2015 to 2018 demonstrate consistent product characteristics across feedstock variability, supporting the proposition that the thermochemistry, rather than the feedstock composition, determines the product.

8. Positioning Constructive Thermochemistry

Three broad disciplines govern the conversion of surface carbon into useful materials: thermochemical processing (the application of heat as the primary conversion driver), chemical and biochemical processing (fermentation, enzymatic conversion, chemical synthesis), and mechanical processing (comminution, densification, extrusion, spinning). Each discipline includes both destructive applications, in which molecular complexity is reduced, and constructive applications, in which it is preserved or increased. Table 1 maps these disciplines against their orientation.

Table 1. Surface Carbon Conversion Disciplines Mapped by Orientation.

Discipline	Destructive Orientation	Constructive Orientation
Thermochemical	Gasification (700 to >1200 °C), Pyrolysis (400 to 800 °C), Torrefaction (200 to 300 °C), HTC (180 to 260 °C, pressurized; primarily hydrolytic despite secondary condensation pathways)	****Constructive DOR**
Chemical / Biochemical	Acid / alkaline hydrolysis, Anaerobic digestion	PLA polycondensation, Cellulose acetylation, Rubber vulcanization
Mechanical Examples ***NOTE: These are processes altering the physical architecture, rather than molecular constructs***	Shredding / grinding, Comminution	Textile weaving / spinning, Extrusion / molding, Papermaking, Lamination / plywood layup

***Cell represents the contribution of this work.*

As shown in Table 1, chemical, biochemical, and mechanical processing of surface carbon each include both destructive and constructive applications. Thermochemical processing, until now, has contained only destructive examples. Every established thermochemical process, from gasification to torrefaction, operates above the destructive threshold and is oriented toward bond-breaking, energy recovery, or feedstock degradation. Thermal wood modification (TWM) is not explicitly referenced in the table, but it is sometimes characterized as a process distinct from torrefaction, particularly in commercial settings. TWM typically targets 200 to 220 °C (and thus is technically mild torrefaction) but it is a process that occupies a range as broad as 180 to 230 °C. Those who investigated TWM provide important confirmation of the chemistry of the lignocellulosic polymers in wood at the very beginning of the destructive process (e.g. hemicellulose degradation). While wood torrefaction aims at improving the properties for combustion purposes, TWM focuses on improving natural wood's properties for structural and aesthetic uses. Thus, while TWM provides important confirmation of early-stage thermochemical changes of wood, it underscores the absence of truly constructive thermochemical methods until the advent of constructive DOR.

Constructive thermochemistry offers the first thermochemical process of a constructive orientation. This positioning clarifies the nature of the contribution. Constructive DOR is not a refinement of pyrolysis, an improvement on torrefaction, or a variant of hydrothermal carbonization. It is the thermochemical analog of PLA polycondensation, cellulose acetylation, and rubber vulcanization: a process that uses surface carbon as a polymeric substrate to build a material of greater complexity than the feedstock. The difference is the conversion discipline. Where those established constructive processes operate through chemical synthesis, fermentation, or catalysis, constructive thermochemistry operates through the controlled application of heat under engineered thermodynamic conditions. It extends the constructive paradigm into a domain where, until now, only destruction was practiced.

9. Next-Phase Characterization and Extended Applications

The DOR process has produced consistent results across more than a decade of continuous development. Composite building materials derived from the process have been fabricated into structural products, machined with standard woodworking tools, fastened with conventional hardware, and exposed to multi-season freeze-thaw weathering without observable degradation. The mechanistic framework presented in this paper accounts for these properties. The author is pursuing spectroscopic characterization as described below that will resolve, at the molecular level, the specific bond architectures and condensation products that the convergent literature and empirical evidence indicate are present.

Spectroscopic confirmation of molecular architecture. The material properties described in Section 7 are consistent with the proposed mechanistic framework. Direct spectroscopic evaluation, targeting C–C linkages from lignin condensation, melanoidin polymeric structures, and the nature of biogenic-synthetic interfacial bonding, will map the molecular architecture underlying the observed properties. The analytical pathways are well understood: 2D-HSQC NMR will map the bonding environment of the product's aromatic and aliphatic carbon networks; FTIR spectroscopy will identify specific functional group transformations; XPS will characterize surface chemistry; gel permeation chromatography will quantify molecular weight distributions; and pyrolysis-GC/MS will fingerprint thermal decomposition profiles.

Additional reaction mechanisms. The four primary mechanisms identified in this paper are those for which the strongest combined operational and literature evidence exists. The author has identified a broader set of reactions that are very likely occurring within the constructive environment: cellulose surface modification at the amorphous-crystalline interface, lipid oxidation and cross-linking within the food waste fraction, radical-mediated coupling between biogenic and synthetic polymer fragments, carbohydrate caramelization reactions operating in parallel with Maillard chemistry, and possible transesterification between organic acid products and hydroxyl-bearing biomass fragments. Confirmation awaits the application of the spectroscopic tools described above.

Platform generality across feedstocks. The constructive thermochemical framework is presented as applicable to the broad class of carbonaceous feedstocks containing natural and/or synthetic polymers. While the primary body of evidence derives from mixed municipal solid waste, which encompasses most major classes of surface carbon polymers, DOR applied to wastewater treatment sludge, narrow organic feedstock streams, and other carbonaceous substrates would be expected to yield consistent constructive outcomes. The consistency of the product across the inherent variability of municipal solid waste is itself evidence of the robustness of the underlying thermochemistry. Systematic characterization across additional feedstock types would further establish the generality of the approach.

Extended temperature regime. The 170 to 190 °C constructive window described in this paper represents the regime of purely constructive thermochemistry, optimized for the production of materials (composites, polymer powders, lumber-alternative products) in which preservation of molecular complexity is the primary objective. A parallel body of investigation by the author has demonstrated that extending the process temperature to 190 to 200 °C produces a material with enhanced energy density and combustion characteristics attributable to the earliest stages of surface carbonization while retaining the constructive foundation. This extended regime is the subject of a forthcoming paper in this series.

Constructive thermochemistry occupies a thermodynamic regime that no prior systematic investigation has addressed. This paper has identified the primary mechanisms operating within that regime, validated each against independent peer-reviewed literature, defined the thermodynamic conditions under which they are activated, and documented the material properties they produce. The molecular-level characterization that modern analytical chemistry can now provide (spectroscopic mapping of bond environments, quantification of condensation products, resolution of cross-linking architectures) will deepen the mechanistic understanding of a process whose operational reality is already established.

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