Adhesion Fundamentals in Spotted Gum (*Corymbia citriodora*)

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**ABSTRACT**

The goal of this project was to advance adhesion science and technology related to the Australian hardwood spotted gum (*Corymbia citriodora*). Plantation-grown spotted gum exhibits poor adhesion properties in comparison with similar woods, such as Gympie messmate (*Eucalyptus cloeziana*). To better understand adhesion differences between these two woods, this research compared and contrasted the surface chemistries of plantation-grown spotted gum and Gympie messmate with a particular focus on sensitivity to thermal deactivation.

Wetting measurements were performed using the sessile drop method. Initial and equilibrium contact angles, time-dependent wetting, and surface energy were determined. Time-dependent wetting and equilibrium contact angles were most informative. Initial contact angles and surface energy calculated with them were misleading and often generated anomalous results.

Heating water-saturated wood to mild surface temperatures (105°C, directly after evaporative cooling) severely deactivated spotted gum but not Gympie messmate. This suggests conventional kiln drying appears unsuitable for spotted gum while amenable for Gympie messmate. Spotted gum likely requires non-aqueous, low surface tension adhesives or aqueous adhesives formulated with surface active wetting agents.

Water-saturation (followed by room-temperature vacuum drying) substantially altered the surface chemistries of both woods, making them more hydrophilic. Consequently, the question was raised of whether a water-spray onto the wood surface prior to adhesive application could improve bonding. If so, this simple, industrially-feasible treatment could prove very beneficial to the wood composites industry. Water-saturation also revealed differences in the two wood’s water permeability, which has implications for adhesive penetration and wood drying and may additionally help explain adhesion differences.

Analysis of the plantation-grown heartwood (inner, middle, and outer heartwood regions) revealed significant wetting differences on spotted gum with only minor differences on Gympie messmate.

The Australian woods were compared to two North American woods—loblolly pine (*Pinus taeda*) and Douglas-fir (*Pseudotsuga menziesii*). Examining water wetting measurements, the Australian and North American woods exhibited some interesting similarities. However, methylene iodide wetting measurements revealed that the Australian woods were quite different from the North American samples studied here.
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1 Introduction and Literature Review

1.1 Introduction.
The goal of this project was to advance adhesion science and technology related to the Australian hardwood spotted gum (*Corymbia citriodora*). According to the Queensland Government, the principal sponsor of this project, plantation-grown spotted gum exhibits poor adhesion properties (McGavin et al., 2013). In comparison, similar woods such as Gympie messmate (*Eucalyptus cloeziana*) exhibit superior adhesion properties. To better understand the adhesion properties of spotted gum, this research was intended to compare and contrast the surface chemistries of spotted gum and Gympie messmate with a particular focus on sensitivity to thermal deactivation. Thermal deactivation, primarily caused by the wood drying process, is a surface phenomenon in which wood surface energy is dramatically reduced thereby resulting in poor adhesion.

Adhesion is fundamental to the wood-based composites industry where the joining of smaller wood elements allows formation of larger, higher-value products. Adhesion generally involves three steps: 1) application of an adhesive (typically a liquid) onto the wood elements, 2) pressure consolidation to close the bond between wood elements, and 3) curing of the adhesive. Within this sequence, the first step, application of the liquid adhesive onto the wood surface is critical. Contact between liquids and solids is referred to as wetting where typically the liquid adhesive forms an angle of contact (i.e. the contact angle) with the solid (Figure 1-1). The nature or quality of wetting is reflected in the contact angle value. Generally, wetting is defined as “favorable” when the contact angle is less than 90° or “unfavorable” when the contact angle is greater than 90°. Wetting quality is dictated by intermolecular forces within the pure liquid, on the solid surface, and at the solid/liquid interface.

![Figure 1-1: Liquid contacting a solid surface; contact angle (θ) is indicated.](image)

1.2 Surface Chemistry.

1.2.1 Surface Tension and Surface Energy.
Intermolecular forces (secondary bonds) are attractive forces acting between neighboring molecules. Within pure, condensed phases (liquids and solids), intermolecular forces cause neighboring molecules to associate or “stick” with one another. The result is cohesion where macroscopic material properties are a manifestation of intermolecular cohesive forces. In
contrast, the macroscopic properties of noncondensed phases (air) are not impacted by intermolecular forces. Where noncondensed and condensed phases meet (i.e. air/liquid or air/solid interfaces), molecules on the surface of condensed phases are deprived of complete stabilization (as compared to bulk molecules) and consequently exhibit an excess energy referred to as surface free energy (Vogler, 1993).

With liquids, surface free energy is an observable contractile force that, via flow, naturally minimizes liquid surface area. A liquid’s contractile tendency is referred to as surface tension and is a measure of cohesion within liquids. Surface tension is a measurable force obtained by determining the work required to increase surface area (Pashley and Karaman, 2004). Techniques for measuring surface tension include du Nouy ring, drop weight, pendant drop, and others (Adamson, 1990).

With solids, that do not flow, the term surface tension is inappropriate. Instead, the term surface free energy (or more-simply surface energy) is appropriate. While liquid surface tension is measurable, solid surface energy cannot be directly measured since solids do not flow. However, solid surface energy can be estimated by measuring the contact angle existing between the solid and a liquid (with known surface tension).

1.2.2. Young’s Equation.

The contact angle (Figure 1-1) represents a balance between the adhesive forces at the solid/liquid interface and cohesive forces within the liquid. The balance is described through Young’s equation and is written as:

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]  

(1-1)

where \( \gamma_{SV} \) is the surface energy of the solid/vapor interface (i.e. solid surface energy), \( \gamma_{SL} \) is the surface energy of the solid/liquid interface (i.e. solid/liquid interfacial energy), \( \gamma_{LV} \) is the surface energy of the liquid/vapor interface (i.e. liquid surface tension), and \( \theta \) is the contact angle. Young’s equation assumes the solid surface is ideally smooth, homogenous, undeformable, and in equilibrium with other phases (Johnson and Dettre, 1993).

When a high energy liquid contacts a low energy solid, cohesive forces within the liquid dominate resulting in a high contact angle. When a low energy liquid contacts a high energy solid, adhesive forces along the solid/liquid interface dominate resulting in a low contact angle. In some cases a liquid will completely wet the solid, thereby spreading over the solid surface and exhibiting a contact angle of zero.

However, Young’s equation alone cannot be used to estimate solid surface energy since both \( \gamma_{SV} \) and \( \gamma_{SL} \) are unmeasurable. Therefore, a second equation is necessary.

1.2.3. Dupre’s Equation.

Dupre’s equation defines the work of adhesion as the work required to disjoin a unit area of solid/liquid interface into respective solid and liquid phases (Berg, 1993):

\[ W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \]  

(1-2)

where \( W_A \) is the work of adhesion needed to separate the solid/liquid interface.
Combining equations 1-1 and 1-2 yields the Young-Dupre equation:

\[ W_A = \gamma_{LV} (1 + \cos \theta) \]  \hspace{1cm} (1-3)

Equations (1-1, 1-2, and 1-3) neglect the equilibrium film pressure \( (\pi_e) \), which represents the reduction in solid surface energy upon adsorption of liquid vapor onto the solid surface (Berg, 1993). However, \( \pi_e \) is considered negligibly small when the contact angle is finite (i.e. contact angle > 0º) (Berg, 1993).

The Young-Dupre equation relates the contact angle directly to the work of adhesion and is the basis upon which subsequent surface energy theories are built. Understanding that solid surface energies may only be estimated, for convenience hereafter the process will be referred to as solid surface energy measurement or determination.

1.2.4. **Determining a Solid’s Surface Energy.**

Initial wetting studies can be attributed to Zisman and co-workers who introduced an empirical theory to measure a solid’s surface energy through contact angle measurements (Johnsen and Dettre, 1993; Good, 1992). This was done by measuring the contact angles of various liquids with known surface tensions on a solid surface. The \( \cos \theta \) is then plotted versus the respective liquid surface tensions. Extrapolation to \( \cos \theta = 1 \) (i.e. \( \theta = 0º \)) indicates the solid’s critical surface energy \( (\gamma_C) \). The \( \gamma_C \) of a solid is considered equal to the surface tension of a liquid for which the contact angle is zero (Good, 1992). This \( \gamma_C \) is not equivalent to the actual surface energy but instead is an estimate of a solid’s surface energy (Good, 1992). Nevertheless, Zisman plots are very useful in characterizing some solid surfaces (Good, 1992).

From Zisman’s work, two subsequent methodologies were developed to determine solid surface energy. The first was the equation-of-state or one liquid theory in which the contact angle from one liquid was used to determine the solid surface energy (Gindl et al., 2001). However, the equation-of-state theory has been highly criticized (Good, 1992; Johnson and Dettre, 1993).

The second methodology was a component theory which estimated solid surface energy based on contributions from components of surface energy, as in nonpolar and polar contributions, and as in acidic and basic contributions to the polar component (Rulison, 1999). Geometric mean and harmonic mean theories are both two-component models which define surface energy as having a nonpolar and a polar component.

A three-component model was developed by subdividing the polar component (mentioned above) into separate Lewis acid and Lewis base component contributions (Good, 1992). This model is known as the Lifshitz-Van der Waals/acid-base (or more simply acid-base) theory and is considered the most complex but also the most informative method of measuring solid surface energy since it reveals nonpolar (dispersive), acidic, and basic qualities (Gindl et al., 2001; Gardner, 1996). The dispersive component characterizes Van der Waals interactions between the solid and liquid (Rulison, 1999). The acid and base components reveal a solid’s ability to interact with complementary polar liquid forces (Rulison, 1999).
1.2.4.1. Lifshitz-Van der Waals/Acid-Base Approach.

Here, the acid-base theory is described using work of adhesion notation. The work of adhesion is separated into dispersive and acid-base intermolecular forces (Berg, 1993):

\[ W_A^{Total} = W_A^{LW} + W_A^{AB} \]  \hspace{1cm} (1-4)

where \( W_A^{Total} \) is the total work of adhesion, \( W_A^{LW} \) is the dispersive component of the work of adhesion, and \( W_A^{AB} \) is the acid-base component of the work of adhesion.

Work of adhesion’s dispersive component follows a geometric combining mean:

\[ W_A^{LW} = 2 \sqrt{\gamma_{SV}^{LW} \gamma_{LV}^{LW}} \]  \hspace{1cm} (1-5)

where \( \gamma^{LW} \) is the dispersive energy component of the solid and liquid.

Work of adhesion’s acid-base component:

\[ W_A^{AB} = 2 \left( \sqrt{\gamma_A^{SV} \gamma_{LV}^{A}} + \sqrt{\gamma_B^{SV} \gamma_{LV}^{B}} \right) \]  \hspace{1cm} (1-6)

where \( \gamma^A \) and \( \gamma^B \) are the acid and base energy components of the solid and liquid.

Combining and rearranging equations 1-4 through 1-6 with the Young-Dupre equation results in:

\[ (1 + \cos \theta) \gamma_{LV} = 2 \left( \sqrt{\gamma_{SV}^{LW} \gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{A} \gamma_{LV}^{A}} + \sqrt{\gamma_{SV}^{B} \gamma_{LV}^{B}} \right) \]  \hspace{1cm} (1-7)

The final equation involves three unknowns \( \gamma_{SV}^{LW}, \gamma_{SV}^{A}, \) and \( \gamma_{SV}^{B} \) and therefore the contact angle of at least three liquids (minimum of two polar liquids and one nonpolar liquid) must be determined. Typically, \( \gamma_{SV}^{LW} \) is determined first using a high-energy nonpolar liquid (van Oss et al., 1988). After which, \( \gamma_{SV}^{A} \) and \( \gamma_{SV}^{B} \) can be determined using high-energy polar liquids with different \( \gamma_{LV}^{A} \) and \( \gamma_{LV}^{B} \) component values (van Oss et al., 1988). Although only a minimum of three liquids is necessary, Gindl et al. (2001) showed increased precision by using five liquids.

1.2.5. Measuring Liquid Contact Angle on a Solid Surface.

Measuring the contact angle is an integral aspect to determining a solid’s surface energy. Techniques for measuring the contact angle on a solid material include the sessile drop, advancing/receding contact angle, and Wilhelmy slide (Adamson, 1990). The measured contact angle value (and consequently the calculated surface energy) highly depends on the method used.

The sessile drop (recall Figure 1-1) is the quickest and most convenient method to measure contact angles. A syringe is used to place a liquid droplet onto a solid surface. The droplet is viewed horizontally from the side through a camera and droplet images are captured and analyzed digitally. On non-porous materials, the sessile drop exhibits a fixed or static contact angle. Porous materials often exhibit dynamic contact angles because capillary forces cause liquid sorption which results in a continual decrease in contact angle over time.

A modification to the sessile drop method is the measurement of the dynamic advancing and receding contact angles. The syringe needle is brought close to the solid surface, almost touching it, and a droplet is dispensed onto the solid surface. The needle tip remains in the
droplet and liquid is continuously pumped into the droplet causing the droplet volume to grow and advance across the solid surface. The contact angle measured at this point is termed the advancing contact angle (Figure 1-2a). When liquid is drawn into the syringe, the droplet volume decreases and the droplet recedes across the surface. The contact angle measured at this point is termed the receding contact angle (Figure 1-2b). Differences between advancing and receding contact angles is known as contact angle hysteresis and indicates a rough and/or chemically heterogeneous solid surface (Pashley and Karaman, 2004). In such cases, the advancing contact angle will always be greater than the receding contact angle (Berg, 1993).

![Figure 1-2: Advancing ($\theta_A$) (a: left) and receding ($\theta_R$) (b: right) contact angles exhibiting contact angle hysteresis.](image)

The Wilhelmy method (Figure 1-3) is unlike the previous two methods. In this method, a thin specimen is immersed into and withdrawn from a liquid of known surface tension by raising and lowering the container containing the liquid. The wetting force exerted on the specimen during the process is measured and the contact angle is indirectly determined.

Wetting force is related to contact angle by (Walinder and Johansson, 2001):

$$F = P\gamma_{LV} \cos \theta - \rho Ahg$$

(1-8)

where $F$ is the wetting force, $P$ is the specimen wetted perimeter, $\gamma_{LV}$ is the liquid surface tension, $\theta$ is the contact angle, $\rho$ is the liquid density, $A$ is the specimen cross-sectional area, $h$ is the immersion depth, and $g$ is the gravitational constant.
1.3. **Wood Surface Chemistry.**
The previous discussion on solid surface chemistry can be applied to the study of wood. Knowledge of wood surface energy is beneficial in manufacturing wood-based composites (e.g. helpful in formulating adhesives that properly wet the wood surface). Wood surface energy is measured as described above, but wood presents several complications, for instance: porosity, three-dimensional anisotropy, biological variation, and mass transfer across the wood/liquid interface (extractives diffusing into the liquid and the liquid diffusing into the wood cell wall) (Liptakova et al., 1998).

1.3.1. **Wood Properties Impacting Wetting Measurements.**
As previously stated, Young’s equation assumes an ideally smooth, homogenous, undeformable surface which is in equilibrium with other phases (Johnson and Dettre, 1993). Wood does not conform to these assumptions as mentioned, since it is an anisotropic, heterogeneous, porous material. Therefore, when applying the Young-Dupre equation to measure wood surface energy, it is necessary to understand the wood surface properties that impact wetting. Wood surface properties are divided into two groups—physical and chemical. Physical properties include morphology, roughness, and porosity. Chemical properties include molecular composition and moisture content.

1.3.1.1. **Physical Properties.**
Surface morphology arises from wood anatomy. Wood is anisotropic which means that its anatomy differs according to its plane of section and direction. Wood contains three planes of section—transverse, radial, and tangential—and three planes of direction—longitudinal, radial, and tangential. Shi and Gardner (2001) studied wetting as a function of grain direction on southern pine and Douglas-fir. Contact angles were significantly lower parallel to the grain direction (i.e. in the longitudinal direction) than perpendicular to it (Shi and Gardner, 2001). This phenomenon was attributed to surface anatomical features. Longitudinal tracheids comprise nearly 90% of softwood volume and are often 100 times longer (parallel to grain direction) than
wide (Wiedenhoeft and Miller, 2005). Therefore, liquids spread more easily parallel to the tracheid lumen than perpendicular to it (Shi and Gardner, 2001).

Surface roughness also impacts wetting. Shaw (1980) found that surface roughness causes unfavorable wetting to be less-favorable (i.e. > 90° becomes > 90° plus). Likewise under favorable wetting, roughness causes a further reduction in contact angle that is not otherwise observed on the corresponding smooth surface. Wood surface roughness arises from the natural anatomy and torn/damaged cell walls caused by mechanical surfaced/machining (Liptakova et al., 1995). Various methods are used to minimize surface roughness and obtain a uniform surface for measurements. Specimen surfaces may be prepared by sanding (Gardner et al., 1991 and Gardner, 1996) or microtoming (Liptakova et al., 1998). Liptakova et al. (1995) compared microtomed and sanded surfaces and found that contact angles were slightly lower on sanded surfaces due to increased surface roughness. Microscopy revealed that microtomed specimens displayed the least amount of surface roughness and were considered most ideal for wetting measurements; sanded surfaces exhibit torn and damaged wood elements which complicate wetting measurements (Liptakova et al., 1995).

Liquid penetration into wood (here described as the micron scale flow into wood cell lumens) is largely dependent on liquid surface tension, viscosity, wood anatomy (i.e. capillary radius as in the Washburn equation [Walinder and Gardner, 1999]), and wood surface energy (Scheikl and Dunky, 1998). For instance, water penetrates more rapidly into spruce and pine earlywood than into the less porous latewood of these species (Scheikl and Dunky, 1998). Furthermore, water penetrates more rapidly into high surface energy woods, and penetration is slower or even prevented on low surface energy woods. Liquid penetration often occurs immediately after wood-liquid contact (Liptakova and Kudela, 1994), and it decreases the contact angle (Meijer et al., 2000).

In addition, liquid bulk sorption into wood particles (nanometer scale swelling of the wood cell wall) often occurs for polar liquids—water, formamide, and methanol, but bulk sorption does not commonly occur for nonpolar liquids—methylene iodide and hexane (Walinder and Gardner, 1999). In addition, liquid vapor moves in advance of the liquid front causing pre-wetting of the wood particles (Walinder and Gardner, 1999). Likewise, when conducting Wilhelmy slide measurements, Gardner et al. (1991) found that water wicked past the water/air/wood interface and partially pre-wetted solid wood, which resulted in lower advancing contact angles when testing speeds were slower.

1.3.1.2. Chemical Properties.
Wood is a heterogeneous material consisting of cellulose, hemicellulose, lignin, and small amounts (usually less than 10%) of extractives. Extractives are low molecular weight molecules that are not chemically bound to the woody matrix. Although all components contribute to surface chemistry, extractives migrate to the wood surface (either naturally or during wood drying processes) and thus significantly influence surface measurements (Hse and Kuo, 1988). Wood extractives can be both polar (e.g. tannins, phenolic compounds, and water soluble oligomeric carbohydrates) and nonpolar (e.g. free and esterified fatty acids and sterols) (Widsten
Nonpolar extractives lower wood surface polarity, consequently reducing polar liquid wetting (Widsten et al., 2006; Chen, 1970). Extractives can be removed from wood through mechanical or chemical processes. Sanding, or even better, lightly planing the wood surface, removed nearly all types of surface extractives (Hse and Kuo, 1988). Treating the surface of tropical woods with acetone, sodium hydroxide, or alcohol-benzene solution can remove surface extractives and consequently result in lower water contact angles (Chen, 1970). Nguyen and Johns (1978) found that extraction with alcohol-benzene solution removed nonpolar extractives from Douglas-fir resulting in improved wetting. However, the same extraction process resulted in no significant change in wetting on redwood, likely due to the low initial nonpolar extractives present in unextracted redwood (Nguyen and Johns, 1978).

The presence of surface extractives poses a problem for surface measurements since they can contaminate the liquids. Liquid extractive contamination lowers liquid surface tension which consequently decreases the contact angle. Walinder and Johansson (2001) determined the effect of liquid extractive contamination by measuring the decrease in liquid surface tension after immersion with non-extracted and extracted wood samples. Liquids were contaminated when immersed with non-extracted samples due to dissolution of extractives in the liquids or presence of non-soluble extractives at the wood/liquid or wood/liquid/air interface (Walinder and Johansson, 2001).

Wood is a hygroscopic material. Meijer et al. (2000) studied the moisture content (MC) effect on spruce and meranti conditioned to 7, 12, and 25% MC. As MC increased, nonpolar methylene iodide and polar formamide contact angles increased (Meijer et al., 2000). Polar water showed a slight decrease in contact angles for spruce but no significant difference in meranti (Meijer et al., 2000). Scheikl and Dunky (1998) also studied MC effects on spruce and pine equilibrated at 3, 8, 12, and 15% MC. In general, increasing MC caused water contact angles to decrease (Scheikl and Dunky, 1998).

### 1.3.2. Contact Angle Acquisition Time.

The contact angle formed by a liquid on a solid wood surface changes as a function of time (Figure 1-4). This change in contact angle over time is caused by wood’s heterogeneous and porous nature. Upon wood-liquid contact, extractives from the wood surface contaminate the liquid and reduce the liquid surface tension (Walinder and Johansson, 2001). Capillary action and liquid penetration into the porous woody matrix also occur. These factors result in a decrease in contact angle over time. After some time, an equilibrium state is obtained in which the contact angle changes very little (Liptakova et al., 1998). The change in contact angle over time is easily observed using the sessile drop method (section 1.2.4).
Figure 1-4: Average change in water contact angle over time on Gympie messmate wood using the sessile drop method; n = 32.

Liptakova studied the change in contact angle over time of water on beech wood and found that three stages were exhibited (Liptakova and Kudela, 1994):

1) Liquid droplet diameter increased due to spreading across the wood surface; droplet height decreased leading to a substantial decrease in contact angle.

2) Droplet diameter remained constant but height decreased. At the end of the second stage, liquid filled all solid surface roughness. Contact angle decreased more slowly and was said to be an equilibrium contact angle.

3) Droplet diameter decreased as the droplet slowly penetrated into the wood substrate. Eventually, contact angle, diameter, and height equaled zero.

The contact angle can change significantly between initial and equilibrium state (Figure 1-4) requiring video capture with careful time measurement. Single contact angles (e.g. used in Young-Dupre’s equation) are generally measured at two time intervals—the instantaneous or initial contact angle immediately after the wood-liquid contact or the equilibrium contact angle at some time interval after the wood-liquid contact.

Due to extractive contamination and liquid penetration, many argue an instantaneous measurement is the only acceptable time at which to measure the contact angle. Nguyen and Johns (1978) measured the contact angle within one second of wood-liquid contact while Nussbaum (1999) measured the instantaneous contact angle.

Liptakova et al. (1998) measured the equilibrium contact angle on several wood species. Equilibrium time was highly variable both between and within wood species (Liptakova et al., 1998). Therefore, equilibrium contact angle time was determined individually for each specimen (Liptakova et al., 1998). Mohammed-Ziegler et al. (2004) applied the Liptakova et al. (1998) method of determining equilibrium contact angles and found an equilibrium contact angle state to occur between three and five seconds after wood-liquid contact. During this time, contact
angle changed very little on all species tested so that equilibrium time did not have to be measured for each specimen. A first-order derivative of the contact angle versus time curve was used to increase accuracy of determining equilibrium contact angle (Mohammad-Ziegler et al., 2004).

### 1.3.2.1. Wetting Model.

Observing the change in contact angle over time supplies information on liquid penetration and spreading. Shi and Gardner (2001) developed a wetting model to quantify the change in contact angle over time. The wetting model is:

\[
\theta = \frac{\theta_i \theta_e}{\theta_i + (\theta_e - \theta_i) \exp[K(\frac{\theta_e}{\theta_e - \theta_i})t]}
\]  

where \(\theta_i\) is the initial contact angle at time 0 sec, \(\theta_e\) is the equilibrium contact angle, \(t\) is time, and \(K\) is the constant intrinsic relative contact angle decrease rate (1/sec). The physical meaning of the \(K\)-value is how fast a liquid spreads and penetrates across or into the wood substrate (Shi and Gardner, 2001). A high \(K\)-value represents a liquid that quickly spreads and/or penetrates into the wood surface, while a low \(K\)-value represents a liquid that slowly spreads and/or penetrates into the wood substrate. A \(K\)-value of zero represents no change between initial and equilibrium contact angles.

![Figure 1-5: Wetting model simulation showing changes in contact angle over time at different K-values.](image)

Since this research addresses heat-induced wood surface deactivation, it is helpful to consider expected trends in liquid \(K\)-value as wood surface energy decreases due to prolonged heating. For example, we could imagine that the simulated curves (in Figure 1-5) reflect the progression from high surface energy (\(K\)-value = 1.000) to low surface energy (\(K\)-value = 0.250) as specimens are heated to various temperatures. The corresponding plot of \(K\)-value versus heating temperature would exhibit a continuous decline in \(K\)-value. However, in this study it will be shown that \(K\)-values do not always continuously decline as a function of heating temperature. For instance, Figure 1-6 shows example \(K\)-value curves as a function of heating temperature.
Curve A exhibits a continuous decline in K-value which is defined here as simple behavior. In contrast, curves B and C each show a discontinuity in K-value (i.e. the K-value does not exhibit a continuous decline as a function of heating). Such a discontinuity may be minor, as in curve B, or dramatic, as in curve C. In either case, such a discontinuity in K-value is defined here as complex behavior where the wood surface exhibits a reversal in the expected wetting behavior as heating temperature increases.

![Graph showing possible changes in liquid K-value as a function of heating temperature.]

**Figure 1-6:** Possible changes in liquid K-value as a function of heating temperature.

The Shi and Gardner wetting model and K-value have been used by others to analyze the wettability of wood surfaces. Qin et al. (2014) used Shi and Gardner’s wetting model to describe wetting behavior of fast-grown poplar after sanding. The K-value allowed for easy quantitative comparison of wetting, but the model’s required initial and equilibrium contact angles were difficult to obtain (Qin et al., 2014). Wang et al. (2015) used the wetting model (K-value) to describe wetting before and after thermal modification and to differentiate between various wood’s wettability following heating.

### 1.3.3. Measuring Wood Surface Energy.

It should be clear that since wood is not an ideal surface (as assumed by Young’s equation), measured wood surface energies are meaningless if the methodology used to obtain the contact angles and the theory used to calculate surface energy are not reported. As previously discussed, the acid-base theory is preferred since information is obtained not only for surface energy but also dispersive, acidic, and basic energy components (Gindl et al., 2001; Gardner, 1996). According to the acid-base theory, in general, the majority of wood’s surface energy is attributed to the dispersive component (Gindl et al., 2001; Gardner, 1996). Within the polar component, the basic contribution is greater that the acidic one (Gindl et al., 2001; Gardner, 1996), although many argue that the acid-base theory overestimates the basic component of many polymer surface energies (Volpe and Siboni, 2000). Since wood is highly variable between species, the exact values for surface energy and its components are dependent on the wood species being sampled (Gardner, 1996).
Wood surface energy may become negatively altered during manufacturing processes involved in the production of wood-based composites. A dramatic decrease in wood surface energy is known as surface deactivation and this severely impairs adhesion.

1.4. **Wood Surface Deactivation.**
A material’s highest possible surface energy is obtained immediately following machining and exposure of a fresh surface. If exposed to the atmosphere, the surface molecular forces (contributing to surface energy) naturally become reduced by particle contamination or from molecular reorientation which leads to a decrease in surface energy (although generally small and occurring slowly over a long period of time) (Marra, 1992). In contrast, a wood surface that experiences a dramatic reduction in surface energy (typically caused by excessive heat) is referred to as deactivated and exhibits impaired adhesion (Vick, 1999).

There are many factors impacting wood surface deactivation, including: light, heat, air, chemical and mechanical treatments (Marra, 1992). Heat-induced or thermal deactivation comprises: primary deactivation from first-time wood drying and secondary deactivation from subsequent heating (e.g. hot-pressing) (Marra, 1992). In the wood-based composites industry, thermal deactivation through high-temperature drying is the predominant cause of wood surface deactivation and occurs through several mechanisms.

Christiansen (1990; 1991) discussed chemical and physical mechanisms by which high-temperature drying could result in thermal deactivation, including: oxidation and pyrolysis of bonding sites, extractive movement to the surface, reorientation of surface molecules, and irreversible micropore closure in the cell wall. Vick (1999) considered extractive movement to the surface as the principle cause of surface deactivation.

A surface that has been thermally deactivated impairs an adhesive’s ability to properly wet, penetrate, and cure on the wood surface (Vick, 1999). Proper adhesive wetting is necessary for good adhesive performance (Chen, 1970). Since sensitivity to thermal deactivation differs among species, understanding a particular species’ sensitivity to thermal deactivation is key to understanding adhesion for that species. This forms the basis for this study.

1.5. **Adhesion Studies with Corymbia spp.**
Very little has been published regarding the bonding characteristics of Corymbia spp. Widsten et al. (2006) found that *Corymbia maculata* exhibited relatively poor adhesion when compared to *Pinus radiata* and seven *Eucalyptus* species. According to Widsten et al. (2006), the poor bonding of *Corymbia maculata* was correlated to its high density and high contents of phenolic and lipophilic extractives. McGavin et al. (2013) found that plantation-grown *Corymbia citriodora* and *Eucalyptus cloeziana* could be used to produce structural veneer products (e.g. plywood and laminated veneer lumber). However, McGavin et al. (2013) found that *Corymbia citriodora* exhibited poor bonding in comparison to *Eucalyptus cloeziana*, and that alkaline phenolic resole resins performed better than melamine-formaldehyde adhesives which were better than moisture-cure polyurethane adhesives.
2 Materials and Methods

2.1 Materials.

2.1.1 Australian Wood Specimen Preparation.
Plantation and non-plantation (native forest) spotted gum (*Corymbia citriodora*) and Gympie messmate (*Eucalyptus cloeziana*) heartwood samples were supplied by the Queensland Government of Australia.

Two plantation trees (12 years old) were sampled for each species. Eight samples (quarter sawn boards ~ 2.5 tangential x 15 radial x 30 longitudinal [cm]) were cut from each tree using the scheme in Figure 2-1. The samples consisted of only heartwood and were not classified by tree height above ground line. Three samples from each tree were randomly selected and machined into three heartwood regions (classified as inner, middle, and outer) by measuring from the pith waste area (Figure 2-1). Beginning from the side of each board nearest the pith, a 15-30 mm section (labeled pith waste area in Figure 2-1) was first removed, and then three 30 mm sections were cut and labeled inner, middle, and outer. From each heartwood region, six specimens were cut. Specimen dimensions were: 13 tangential x 13 radial x 27 longitudinal (mm). Only defect-free specimens were used. Specimens were stored at room temperature in sealed plastic bags.

![Figure 2-1: Depiction of specimen sampling from plantation grown specimens used in this study.](image)

Non-plantation heartwood samples were not classified by heartwood region. Non-plantation specimens were cut into dimensions 13 tangential x 13 radial x 27 longitudinal (mm). Only defect-free specimens were used. Specimens were stored at room temperature in sealed plastic bags.

2.1.1.1 Import Requirements.
Australian (plantation and non-plantation) woods were required to undergo treatment in order to be imported into the United States. Treatment consisted of heating (60ºC core temperature maintained for 24 hr) and fumigating with methyl bromide (120 g/m³ dosage rate exposure for 16 hr at a minimum sample temp of 15.1ºC).
2.1.2. **North American Wood Specimen Preparation.**

Two loblolly pine (*Pinus taeda*) non-plantation trees (~40 years old from Critz, Virginia) and one Douglas-fir (*Pseudotsuga menziesii*) non-plantation tree (~47 years old from Benton County, Oregon) were obtained. Samples (~2.5 tangential x 15 radial x 30 longitudinal [cm]) of mature heartwood were taken between 4.9 and 7.3 m (tree height) above ground line and stored at 21°C and 65% relative humidity (wood equilibrium MC of 12%). Three samples were randomly chosen and machined into specimen dimensions: 13 tangential x 13 radial x 27 longitudinal (mm). Only defect-free specimens were used. Specimens were stored at room temperature in sealed plastic bags.

2.1.3. **Specimen Variation.**

Care was taken to prepare perfectly tangential surfaces (the experimental surface), yet some variation resulted. Two separate variations were recorded: 1) the average grain deviation from the longitudinal direction (Figure 2-2, Table 2-1), and 2) the average tangential surface deviation as viewed from the cross-section or end-grain (i.e. the angle between the experimental surface and a true, ideal tangential surface) (Figure 2-3, Table 2-2). For each species/growth combination, nine specimens were randomly measured. The deviations occurred in both directions and are listed as +/-.

![Figure 2-2: Grain deviation angle (θ) from the longitudinal direction.](image)

<table>
<thead>
<tr>
<th>Species</th>
<th>Plantation Wood (AVG)</th>
<th>Plantation Wood (Std dev.)</th>
<th>Non-plantation Wood (AVG)</th>
<th>Non-plantation Wood (Std dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>spotted gum</td>
<td>3.3</td>
<td>2.8</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Gympie messmate</td>
<td>1.2</td>
<td>1.5</td>
<td>2.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Table 2-2: Tangential Surface Deviation Angle (+/−) as Viewed from the Cross-section.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plantation Wood</th>
<th></th>
<th>Non-plantation Wood</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(AVG)</td>
<td>(Std dev.)</td>
<td>(AVG)</td>
<td>(Std dev.)</td>
</tr>
<tr>
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<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
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<td>--</td>
<td>--</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

2.1.4. Surfacing.

A SwapTop Flat Lap grinder with 15.2 cm diameter diamond grit disks from Inland Craft Products was used to surface specimens. Tangential surfaces were sanded in grit order: 100, 170, 275, 325, 600, and 1200. Sanding times were as follows: grits 100-170 (four, 10 sec cycles) and grits 275-1200 (two, 10 sec cycles). Specimens were rotated 180º between each cycle to ensure complete, even sanding. Sanding pressure was controlled by hand, but in a systematic fashion to avoid over-heating the wood.

For each species/growth combination, batches of six specimens were sanded in random order at each grit size. Specimens were cleaned with N₂ (50 psi) by blowing each surface for 2-3 sec. Diamond disks were cleaned with soap and water and rinsed with acetone. Separate disks were used for each species to eliminate cross-contamination.

2.1.4.1. Sanded Specimen Surface Roughness.

Specimen tangential surface images (plantation spotted gum) were taken using scanning electron microscopy (Neo Scope JCM-5000) after 1200 grit sanding, cleaning with N₂ (50 psi) for 2-3 sec, and drying (40ºC, 2 days).

2.1.4.2. Sanded Specimen Surface Temperature.

Specimen surface temperature (non-plantation spotted gum and Gympie messmate) was measured 1-2 sec after sanding at each grit using a thermal FLIR E5 infrared camera (thermal sensitivity < 0.10ºC). Four measurements were conducted for each species at each grit.

2.1.5. Heat-treatment from Dry State.

Non-plantation spotted gum and Gympie messmate were heat-treated from a dry state (i.e. MC < 2%). Specimens were surfaced (section 2.1.3) and then dried in desiccators (separated by species) at room temperature and atmospheric pressure using phosphoric pentoxide (P₂O₅) and...
N₂ blanket. Each day, P₂O₅ was replenished and three vacuum cycles (15 min vacuum [0.15 mmHg], then backfilled to 1 atm with N₂) were applied. Specimens were dried until MC < 2% (~ 3 days).

Dried specimens were resurfaced (section 2.1.3) using only grits 325, 600, and 1200. Specimens were cleaned with N₂ (50 psi) by blowing each surface for 2-3 sec.

Specimens were individually wrapped in clean aluminum foil and heated in a preheated 200°C convection oven to a desired time—control (i.e. unheated), 15, 30, or 60 min. Specimens were then cooled (to room temperature) in a desiccator for 1.5 hr under N₂ blanket with P₂O₅. Cooled specimens were removed from the desiccator, unwrapped, and subjected to surface analysis.

2.1.6. Heat-treatment from Water-saturated State.
Spotted gum, Gympie messmate, loblolly pine, and Douglas-fir were heat-treated from a water-saturated state (i.e. MC > fiber saturation point). Specimens were surfaced (section 2.1.3) and then water-saturated to a desired MC (Table 2-3) using cyclic vacuum/pressure soak.

<table>
<thead>
<tr>
<th>Species</th>
<th>Desired Moisture Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>plantation spotted gum/Gympie messmate</td>
<td>50ᵃ</td>
</tr>
<tr>
<td>non-plantation spotted gum/Gympie messmate</td>
<td>35ᵃ</td>
</tr>
<tr>
<td>loblolly pine</td>
<td>33ᵇ</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>37ᵇ</td>
</tr>
</tbody>
</table>

ᵃ. Supplied by Queensland government sponsor.

Specimens were placed into individual beakers with approximately 25 mL water (HPLC grade). The beakers (containing the wood/water) were placed into desiccators (separated by species). Cyclic vacuum/pressure soak (15 min aspirator vacuum, then backfilled to 1 atm with N₂) was conducted daily until the desired MC was obtained.

Prior to weighing, water-saturated specimen surfaces were blown for 2-3 sec with N₂ (50 psi) to remove surface water. Water-saturated specimen MC was determined as follows:

\[ MC = \frac{\text{wet weight} - \text{O.D. weight}}{\text{O.D. weight}} \times 100 \]  

(2-1)

where MC was the specimen moisture content after water-saturation, wet weight was the specimen weight after water-saturation and O.D. weight was the estimated specimen oven dry weight determined through equation 2-2.

Specimens were water-saturated from approximately 8% MC, so the oven dry weight was not known. The oven dry weight was estimated as follows:
\[ O.D. \text{ weight} = \frac{\text{specimen weight}}{(\frac{8}{100} + 1)} \]  

where \text{specimen weight} was the weight at 8\% MC prior to water-saturation.

Water-saturated specimens were heated in a preheated 200°C convection oven to a desired surface temperature—control (i.e. unheated), 98, 105, 130, 165, or 192°C. Surface temperature was measured with an Omega HH82 digital thermometer with an Omega fine wire thermocouple. The thermocouple wire was wrapped in Teflon tape and inserted into a 1.6 mm diameter hole drilled underneath the specimen’s non-sanded tangential surface (Figure 2-4). The hole’s outer circumference was 1 mm from the tangential surface, and the hole continued halfway down the specimen length (a jig ensured consistent positioning across all specimens).

![Specimen with inserted thermocouple](image)

Following heating, specimens were immediately wrapped in aluminum foil (leaving end-grain uncovered) and subsequently dried in desiccators (separated by species) at room temperature and atmospheric pressure using \( \text{P}_2\text{O}_5 \) and \( \text{N}_2 \) blanket. Each day, \( \text{P}_2\text{O}_5 \) was replenished and three vacuum cycles (15 min vacuum [0.15 mmHg], then backfilled to 1 atm with \( \text{N}_2 \)) were applied. Specimens were dried until MC \(< 2\% (~11\text{ days})\). Dried specimens were removed from the desiccator, unwrapped, and subjected to surface analysis.

### 2.1.7. Liquids for Surface Analysis.
Water (HPLC-grade), methylene iodide (reagent plus, \( \geq 99.0 \% \) pure), and formamide (A.C.S. grade, \( \geq 99.5 \% \) pure) were used as received from Sigma-Aldrich. Liquids were transferred to 10 mL amber bottles with rubber tops (liquid replaced monthly) to allow syringe loading without liquid/air contact. Light-sensitive methylene iodide was further protected by wrapping the amber bottle in aluminum foil.

### 2.2. Methods.

#### 2.2.1. Wetting and Surface Energy Measurements.
Contact angle measurements were conducted to measure wood surface energy and determine change in contact angle over time (time-dependent wetting).
2.2.1.1. Contact Angle Procedure.
The sessile drop method was used with two drop transfer techniques (growing drop and static drop). Non-plantation Australian woods were sampled with the growing drop technique; plantation Australian and North American woods were sampled with the static drop technique.

A First Ten Angstroms (FTA) 200 dynamic contact angle analyzer was used to place six droplets (two of each liquid) onto the specimen tangential surface within 5 mm of the edge (so droplet and baseline were in focus) (Figure 2-5). No distinction between earlywood and latewood was made for spotted gum and Gympie messmate. Loblolly pine and Douglas-fir earlywood regions were sampled. Measurements were conducted at ambient conditions without temperature or relative humidity control.

Droplet placement and order (Figure 2-5) was identical on all specimens: 1st) water, 2nd) methylene iodide, 3rd) formamide. Batches of six specimens (same species/growth type) were sampled with all three liquids in approximately one hour. Liquid sampling was done in stages (e.g. all specimens in a batch were sampled using water before sampling with methylene iodide, etc). Between liquid sampling, the droplet was carefully removed from the surface with a Kimwipe and the specimen was stored in an individual beaker covered with Parafilm.

A two-axis stand from Thor Labs leveled the specimen to achieve a horizontal baseline (front-to-back and side-to-side). The camera was perpendicular to the specimen’s longitudinal direction and level with the sampled tangential surface (i.e. a 0º lookdown camera angle) (Figure 2-5).

2.2.1.2. Contact Angle Acquisition.
Contact angle images were captured using a Point Grey Research Firefly MV camera with a Navitar lens and analyzed using FTA 32 Version 2.1 software. Contact angles were the average of both droplet sides using a spherical fit model (Figure 2-6).
Contact angles were measured initially (i.e. first clear image) and every 0.1 sec until 10 sec. Initial contact angle acquisition time varied for liquid and technique (Table 2-4).

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Growing Drop Technique (sec)</th>
<th>Static Drop Technique (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Formamide</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Methylene iodide</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
**Table 2-5:** Liquid Surface Tension and Energy Components (mJ/m²).

<table>
<thead>
<tr>
<th>Liquids</th>
<th>( \gamma_L )</th>
<th>( \gamma_{LW} )</th>
<th>( \gamma_{AB}^{AB} )</th>
<th>( \gamma_A )</th>
<th>( \gamma_B^B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water ( \text{H}_2\text{O} )</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Formamide ( \text{HCONH}_2 )</td>
<td>58.0</td>
<td>39.0</td>
<td>19.0</td>
<td>2.3</td>
<td>39.6</td>
</tr>
<tr>
<td>Methylene Iodide ( \text{CH}_2\text{I}_2 )</td>
<td>50.8</td>
<td>50.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

2.2.2. **Light Microscopy.**

Wood tyloses vessel occlusion (non-plantation/plantation spotted gum and Gympie messmate) was visually examined by obtaining light microscopy images of the tangential surface (Nikon SMZ-1500 stereoscope light microscope with a Nikon DS-Fi1 camera).

Non-plantation specimens were microtomed using a Leica SM-2500 microtome fitted with a stainless steel “C” profile knife. Plantation specimens (from the middle heartwood region) were microtomed using a sliding microtome fitted with OLFA replaceable knives.

2.2.3. **Soxhlet Extraction.**

Wood extractives (non-plantation spotted gum and Gympie messmate) were determined using Soxhlet water extraction followed by ethanol extraction according to the National Renewable Energy Laboratory (NREL) procedure (Sluiter et al., 2008). Specimens were milled with a Wiley mill to pass through a 20 gauge mesh. Two replications were conducted per wood type.

2.2.4. **Density.**

Oven dry density (non-plantation spotted gum and Gympie messmate) was determined. Six specimens (~19 tangential x 13 radial x 38 longitudinal [mm]) per species were randomly selected from the samples and dried in a 105°C oven for 48 hours (additional drying for 24 hours resulted in < 0.5% weight loss). Volume was measured using calipers (two measurements were taken per plane of direction and averaged).

2.2.5. **Data Analysis.**

All data was processed in Microsoft Office Excel 2013. Graphing was conducted in OriginPro 2015. In figures, \( S \)=number of specimens; \( n \)=number of observations over \( S \). In time-dependent wetting curves, some data points and error bars were removed for clarity.

One-way ANOVA with Tukey test means comparison \((\alpha=0.05)\) was conducted to determine grit size and heat-treatment impact on contact angle. Note that in most cases data did not fit ANOVA assumptions of normal distribution and equal variance. This was likely caused by the high variability of wood material and was briefly discussed in Appendix B.

Two sample t-test with Welch correction factor (since equal variance not assumed) was conducted to determine differences in drop transfer technique and heartwood region sensitivity to thermal deactivation.
3 Methods Development
The methods development chapter describes the development and evolution of the techniques used in this study. Among the variety of topics described, note that this section discusses the effects of wood thermal deactivation when heating wood from a dry state. This was the first thermal treatment method used in this study. The results from this preliminary study suggested that more appropriate specimen treatments were needed.

3.1 Specimen Surfacing.
Specimens were surfaced identically to achieve uniform, minimal surface roughness. Liptakova et al. (1995) found that microtoming produced the least surface roughness and was considered the most ideal surfacing method. However, in this study, specimens were unsuccessfully microtomed—iron in the stainless steel knife reacted with wood extractives to form a dark blue stain which was suspected to have altered the wood surface chemistry (Figure 3-1). Use of a tungsten carbide knife was examined but was not compatible with the microtome used in this study. Therefore, diamond grit sanding was adopted as the surfacing method.

![Figure 3-1: Staining (shown on knife) occurred while microtoming non-plantation spotted gum.](image)

3.1.1 Sanding Impact on Liquid Spreading.
Shi and Gardner (2001) found that liquids spread more parallel (as opposed to perpendicular) to the grain which resulted in lower contact angles. Likewise, sanding direction could impact liquid spreading and contact angle. After sanding with 1200 grit, sanding scratches were observed with scanning electron microscopy (Figure 3-2).
Since sanding was performed with a circular disk, scratch direction was not parallel to grain (longitudinal) direction (Figure 3-3). Therefore, drop location could impact contact angle. This effect was not tested but was accepted as systematic error due to the systematic drop placement described previously (chapter 2, Figure 2-5).

Figure 3-3: Sanding scratch relation to grain direction on tangential surface.

3.1.2. Sanding Grit Impact on Contact Angle.
Diamond disk grit and particle sizes are listed in Table 3-1. The effect of grit size on contact angle was determined by sanding specimens to final grits 325, 600, or 1200 and then conducting surface analysis (Figure 3-4).
Table 3-1: Diamond Disk Particle Size.

<table>
<thead>
<tr>
<th>Grit</th>
<th>Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>149-125</td>
</tr>
<tr>
<td>170</td>
<td>88-74</td>
</tr>
<tr>
<td>275</td>
<td>53-45</td>
</tr>
<tr>
<td>325</td>
<td>45-37</td>
</tr>
<tr>
<td>600</td>
<td>30-29</td>
</tr>
<tr>
<td>1200</td>
<td>18-12</td>
</tr>
</tbody>
</table>

A one-way ANOVA test with Tukey test means comparison ($\alpha=0.05$) was conducted to compare effects of grit size for both species. Grit size did not significantly impact contact angle values for the three liquids (complete statistical results presented in Appendix C). However, water contact angles appeared lowest on specimens surfaced to 1200 grit. Low contact angles reflect high wood surface energy and were considered more desirable. Therefore, 1200 grit was adopted as the final surfacing prior to surface analysis.

![Figure 3-4: Grit size comparison. Non-plantation spotted gum and Gympie messmate. Error bars represent ± 1 standard deviation.](image)

3.1.3. **Surface Heating from Sanding.**

Significant surface heating during the sanding process could mask subsequent heat-treatment effects. Therefore, specimen temperature was measured after sanding at each grit (Figure 3-5).
Temperatures were highest after sanding at low grits but decreased when sanding at high grits (Figure 3-6). Nevertheless, the maximum surface temperature (after 100 grit sanding) was less than subsequent heat-treatment temperatures, so sanding was not a concern for its impact on the results.

As seen in Figure 3-6, Gympie messmate surface temperature was higher than spotted gum when sanded at the same grit. We would expect the denser wood to generate the higher surface temperature. However, the opposite was true, since non-plantation spotted gum was found to be slightly more dense (1.11 g/cm\(^3\) ± 0.02) than non-plantation Gympie messmate (1.00 g/cm\(^3\) ± 0.03).

A possible explanation for differences in surface temperature may be in the wood’s thermal conductivity. Wood thermal conductivity increases with increasing density and MC (Wood
Handbook, 2010). A higher thermal conductivity could mean the wood was able to dissipate heat more readily into the bulk material, resulting in a lower surface temperature. As previously stated, spotted gum was denser than Gympie messmate. Spotted gum also contained a slightly higher MC (7.9% ± 0.2) than non-plantation Gympie messmate (6.5% ± 0.6) (determined by TGA [Appendix A, Figure 7-1]). Although thermal conductivity was not measured for the two species, the higher density and MC of spotted gum suggested its thermal conductivity was possibly greater than that of Gympie messmate which could explain differences in surface temperature following sanding.

It is important to note that specimens were sanded by hand but in a systematic fashion to avoid variation in imposed sanding pressure. Therefore, operator variation in sanding pressure may have contributed to wood surface temperature differences; however, since both woods exhibited similar behavior at high grits (325 – 1200), operator variation doesn’t appear to explain these differences.

3.2. Wetting Measurements.
3.2.1. Comparison of Sessile Drop Measurements.
The sessile drop method was used with two drop transfer techniques: growing drop and static drop.

In the growing drop technique, a droplet was dispensed at a fixed rate and fell from the needle tip (due to gravity) at approximately the same time the droplet touched the specimen (Figure 3-7a). However, the droplet was subject to excess momentum from gravity and syringe pump rate. This excess momentum could cause additional spreading and lower contact angles.

In the static drop technique, a droplet of fixed volume was dispensed onto the needle tip. Once pumping was complete, the specimen was raised to “pluck” the droplet from the needle tip (Figure 3-7b), eliminating excess momentum from gravity and syringe pump rate.

Figure 3-7: Growing drop technique (a: left); static drop technique (b: right).
The three liquid initial drop diameters were nearly identical within each technique (Table 3-2). This was desired, since each liquid droplet would “experience” similar wood surface anatomy (Figure 3-8). Furthermore, the static drop technique produced equal-volume drops, which was desired since drop volume impacts the contact angle (Good and Koo, 1979).

<table>
<thead>
<tr>
<th>Probe Liquid</th>
<th>Growing Drop</th>
<th>Static Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drop Volume</td>
<td>Initial Drop Diameter</td>
</tr>
<tr>
<td>Water</td>
<td>6.0 µL</td>
<td>3.0 mm</td>
</tr>
<tr>
<td>Formamide</td>
<td>3.5 µL</td>
<td>3.0 mm</td>
</tr>
<tr>
<td>Methylene iodide</td>
<td>1.0 µL</td>
<td>2.0 mm</td>
</tr>
</tbody>
</table>

Figure 3-8: Droplet diameter examples on non-plantation spotted gum sanded to 1200 grit.

Growing drop and static drop techniques were conducted using water (Figure 3-9) and statistically compared using a two sample t-Test with Welch correction factor ($\alpha=0.05$). No significant differences were detected between techniques (Appendix C), even at 165°C and 192°C surface temperatures. This was possibly due to a small sample size and unequal variance. However, the static drop technique appeared to produce higher contact angles which agreed with the assumption that the technique was less susceptible to spreading from excess momentum. For this reason (and the consistent drop volume [recall Table 3-2]), the static drop technique was chosen as the preferred procedure.
3.2.2. **Time-dependent Wetting and K-value.**

The change in contact angle over time (time-dependent wetting) is caused by wood heterogeneity and porosity (Figure 3-10). Upon wood-liquid contact, wood extractives likely contaminate the liquid and change its surface tension (Walinder and Johansson, 2001). Capillary action and liquid penetration into the porous woody matrix also probably occur. These factors cause a decrease in contact angle over time. After some time, an equilibrium state is obtained in which the contact angle changes very little over time (Liptakova et al., 1998). In this study, equilibrium state was defined as occurring at 10 sec for all three liquids. As shown in Figure 3-10, data suggests equilibrium was achieved for methylene iodide and nearly reached for formamide and water.

![Figure 3-9: Comparison of static drop and growing drop techniques on plantation spotted gum. Error bars represent ± 1 standard deviation.](image)

![Figure 3-10: Time-dependent wetting on non-plantation spotted gum (water-saturated, then dried). Error bars represent ± 1 standard deviation.](image)
The wetting model K-value was used to quantify time-dependent wetting and described the rate of liquid spread and penetration across or into the wood substrate (Shi and Gardner, 2001). A high K-value indicates a liquid that quickly spreads and/or penetrates into the wood surface, while a low K-value indicates a liquid that slowly spreads and/or penetrates into the wood substrate. A K-value of zero indicates no change between initial and equilibrium contact angles. Simulation curves were developed to represent time-dependent wetting at different K-values (Figure 3-11).

![Figure 3-11: Wetting model simulation and corresponding K-values assuming initial contact angle (90º) and equilibrium contact angle (40º).](image)

3.3. Heating Non-plantation Wood from a Dry State.
Non-plantation spotted gum and Gympie messmate were heated from a dry state (MC < 2%). The sensitivity to thermal deactivation was examined using initial contact angles and time-dependent wetting. It is generally expected that heating wood to higher and higher temperatures (or heating for longer times) leads to a reduction in surface energy. Consequently, a polar liquid (e.g. water) is expected to exhibit higher initial contact angles and lower K-values (i.e. impaired time-dependent wetting) as heating severity increases. However, a nonpolar liquid (e.g. methylene iodide) is expected to exhibit reversed trends or at least a trend quite different from that of water.

3.3.1. Initial Contact Angles.
Initial contact angles were measured for the three liquids at each heat-treatment (Figure 3-12). A one-way ANOVA test with Tukey test means comparison (α=0.05) was conducted to compare effects of heating for each species. Complete statistical results are presented in Appendix C.

Polar liquid (water and formamide) initial contact angles on both woods exhibited no significant change due to heating (one-way ANOVA results; spotted gum p-value: 0.08 and 0.56 for water and formamide, respectively; Gympie messmate p-value: 0.13 and 0.17 for water and formamide, respectively).
In contrast, nonpolar methylene iodide initial contact angles exhibited a significant change due to heating on both woods (one-way ANOVA p-value: 0.01 and 0.00 for spotted gum and Gympie messmate, respectively) (the means comparison test results are presented in Appendix C). However, as seen in Figure 3-12 the magnitude of the differences was quite small.

Generally speaking, the initial contact angles presented in Figure 3-12 revealed little insight. The initial contact angles did reflect differences in liquid surface tension (i.e. the highest contact angles occurred with water, the lowest with methylene iodide, and formamide in between). However, Figure 3-12 suggested that initial contact angles would not provide a useful comparison of the wood’s sensitivity to thermal deactivation. Consequently, time-dependent wetting was investigated next.

![Figure 3-12](image.png)

**Figure 3-12:** Initial contact angles on non-plantation spotted gum and Gympie messmate as a function of heating time (min) at 200°C. Error bars represent ± 1 standard deviation.

### 3.3.2. Time-dependent Wetting.

Time-dependent wetting was determined for each liquid at each heat-treatment and was quantified using the wetting model K-value. In contrast to initial contact angles, the time-dependent wetting behavior of each liquid was somewhat more informative and more in agreement with the expectations.

#### 3.3.2.1. Polar Liquid Time-dependent Wetting.

Water time-dependent wetting was more favorable on Gympie messmate than spotted gum (i.e. larger decrease in contact angle over time [Figure 3-13a,b] and larger K-value [Figure 3-14]). For both woods, water time-dependent wetting was most favorable on unheated specimens and became progressively worse due to heating, as evidenced by the reduction in K-value (Figure 3-14). Unexpected, though, was that Gympie messmate exhibited a dramatic reduction in K-value at short heating times (15 min) while spotted gum exhibited a more-gradual reduction in K-value due to heating.

Time-dependent wetting and K-values indicated that both woods became severely deactivated due to heating. Recall that this was not observed when using initial contact angles (Figure 3-12).
Not reflected in the K-values (but noticed in the time-dependent wetting) was the more complex behavior seen in spotted gum due to heating. For spotted gum, the 60 min heating curve crossed the unheated curve. In contrast, the unheated Gympie messmate curve was below all curves associated with heating. This behavior was not depicted in the K-value plot (Figure 3-14) which suggested that consideration of the K-value alone could be misleading.

![Figure 3-13](image1.png)

**Figure 3-13:** Water time-dependent wetting on non-plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of heating time (min) at 200°C. Error bars represent ± 1 standard deviation.

![Figure 3-14](image2.png)

**Figure 3-14:** Water K-value on non-plantation spotted gum and Gympie messmate as a function of heating time (min) at 200°C.

As expected, formamide time-dependent wetting was more favorable than that of water. Furthermore, formamide time-dependent wetting was more favorable on unheated spotted gum than unheated Gympie messmate (Figure 3-15a,b; 3-16). As heating times increased, both woods exhibited less favorable time-dependent wetting. It was noticed that Gympie messmate exhibited a minor degree of complexity in that the 30 min heating curve was mostly below that for the 15 min heating curve and opposite of the general expectation. This was reflected in a minor discontinuity seen in the Gympie messmate K-values (i.e. the K-values did not exhibit a continuous decline due to heating).
Figure 3-15: Formamide time-dependent wetting on non-plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of heating time (min) at 200°C. Error bars represent ± 1 standard deviation.

Figure 3-16: Formamide K-value on non-plantation spotted gum and Gympie messmate as a function of heating time (min) at 200°C.

3.3.2.2. Nonpolar Liquid Time-dependent Wetting.
Methylene iodide time-dependent wetting was more favorable on unheated spotted gum as compared to unheated Gympie messmate (Figure 3-17a,b; 3-18). As heating times increased to 30 min, both woods showed gradual reductions in methylene iodide time-dependent wetting. However, both woods exhibited an interesting complexity in that wetting trends were reversed at the longest heating time of 60 minutes. This complexity was clearly seen as a large discontinuity in K-values and was more evident in spotted gum (Figure 3-18).
3.4. Heating Wood from a Water-saturated State.

Heating from a dry state showed that both woods exhibited some sensitivity to thermal deactivation. These changes were hardly apparent when considering the initial contact angles but were much more obvious when considering time-dependent wetting and the corresponding K-values. Heating from a dry state also revealed that Gympie messmate exhibited less-favorable wetting and greater thermal sensitivity in comparison to spotted gum, exactly opposite of the expectation.

However, heating wood from a dry state misrepresents industrial practices and neglects a principal cause of thermal deactivation. In the wood products industry, veneer sheets are dried from (or near) a green moisture content (i.e. a MC above fiber saturation point [FSP] and corresponding to a freshly cut piece of wood [Hoadley, 1990]). Above FSP, wood contains free water (liquid or vapor in the cell lumens) and bound water (chemically bound within the cell wall) (Wood Handbook, 2010). During drying, free water moves to the surface, bringing with it...
extractives that are deposited on the surface (when water evaporates) resulting in an extractive-rich wood surface (Hse and Kuo, 1988). Extractives on the wood surface are regarded as the principal cause of surface deactivation and poor liquid wetting (Vick, 1999). Therefore, in order to more accurately represent industrial practices and allow for extractive movement, a method was developed to heat wood from a water-saturated state.

3.4.1. Percent Water-soluble Extractives.
Soxhlet (water and subsequent ethanol) extractions indicated a high concentration of polar extractives in both species (Table 3-3). When wood is dried from a water-saturated state, it is obvious how water-soluble extractives could be moved to the wood surface. However, we should expect that nonpolar extractives could also be moved to the wood surface either through steam distillation or as surface active contaminants in liquid water.

<table>
<thead>
<tr>
<th>Table 3-3: Water and Ethanol Soluble Extractives.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-plantation Species</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>spotted gum</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Gympie messmate</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

a. Estimate, flask broke before final measurement.

3.4.2. Evaporative Cooling.
Heating wood from a water-saturated state allowed for evaporative cooling (another phenomenon impacting thermal deactivation) (Figure 3-19a,b). As wood was dried, liquid water was first removed. Above FSP, liquid water moved to the surface and was evaporated, causing evaporative cooling of the wood surface which “protected” the wood surface from reaching a high temperature where thermal deactivation could ensue (Christiansen, 1990). Surface temperatures of 98 and 105°C occurred immediately before and after evaporative cooling, respectively.

Once liquid water was removed, the more strongly-held bound water moved to the surface in the form of vapor, which did not produce the same cooling effect and consequently the wood surface temperature increased (Christiansen, 1990). Wood thermal deactivation has been shown to be promoted by high drying temperatures, long drying times, and low wood moisture content (Christiansen, 1990). For these reasons, surface temperatures (130, 165, and 192°C) were chosen beyond evaporative cooling where thermal deactivation was possibly more severe.
Figure 3-19: Non-plantation spotted gum surface temperature as a function of heating time during 200°C treatment (a: left) and adjusted axis to emphasize stage of evaporative cooling (b: right). Error bars represent ± 1 standard deviation.

3.4.3. Wood Water-permeability.
Samples were received from the project sponsor at approximately 8% MC and were water-saturated to a MC reflective of the species’ green MC. The saturation process revealed differences in wood water-permeability (Figure 3-20).

Non-plantation spotted gum was less water-permeable than non-plantation Gympie messmate, taking approximately twice as long to reach 35% MC. Similarly, plantation spotted gum was less water-permeable than plantation Gympie messmate, taking approximately three times as long to reach 50% MC. Non-plantation wood was less water-permeable than plantation wood.

These observations agree with Redman et al. (2012) who found that non-plantation spotted gum was much less permeable than several non-plantation Eucalyptus species (Gympie messmate was not included in the study but is a Eucalyptus).
One possible explanation for permeability differences was vessel occlusion. Tyloses are bubble-like structures (arising from parenchyma cells) that protrude into heartwood vessel lumens, restricting liquid flow in certain hardwoods (Hoadley, 2000; Wood Handbook, 2010).

Light microscopy of spotted gum and Gympie messmate (non-plantation [Figure 3-21; 3-22] and plantation [Figure 3-23; 3-24]) revealed the presence of tyloses in both woods. It was believed that tyloses vessel occlusion might explain (or partially explain) the differences in water-permeability. However, the microscopy conducted in this study was insufficient to make such a claim.

Since liquid permeability has implications for drying operations and for adhesive penetration, further analysis of the permeability of these two woods could be valuable.

**Figure 3-20:** Spotted gum and Gympie messmate increase in moisture content during water-saturation. Error bars represent ± 1 standard deviation.

**Figure 3-21:** Tyloses vessel occlusion in non-plantation spotted gum (a: left); Gympie messmate (b: right).
3.4.4. Water-saturation Impact on Control Specimens.
To determine the effects of water saturation on wood surfaces, non-plantation specimens were subjected to surface analysis with respect to the following groupings: 1) unsaturated, vacuum
dried to MC < 2% using no heat (room temperature and atmospheric pressure using P₂O₅ and N₂ blanket), and 2) water saturated as described previously and subsequently vacuum dried with no heat to MC < 2% (as in 1).

For both woods following saturation, water time-dependent wetting became more favorable, indicating that the surface became more hydrophilic (Figure 3-25a,b); however, the change was greater on Gympie messmate than on spotted gum.

The two woods exhibited different behaviors when sampled with formamide. Formamide time-dependent wetting became less favorable on spotted gum but more favorable on Gympie messmate following saturation (Figure 3-26a,b).

Figure 3-25: Water time-dependent wetting on non-plantation spotted gum (a: left); Gympie messmate (b: right) showing effect of water-saturation. Error bars represent ± 1 standard deviation.

Figure 3-26: Formamide time-dependent wetting on non-plantation spotted gum (a: left); Gympie messmate (b: right) showing effect of water-saturation. Error bars represent ± 1 standard deviation.
For both woods following saturation, methylene iodide time-dependent wetting became less favorable, indicating that the surface became more hydrophilic (Figure 3-27a,b). As observed with water sampling, this change was more evident on Gympie messmate.

![Graphs showing wetting properties](image)

**Figure 3-27**: Methylene iodide time-dependent wetting on non-plantation spotted gum (a: left); Gympie messmate (b: right) showing effect of water-saturation. Error bars represent ± 1 standard deviation.

Following saturation, the water used to saturate both woods became slightly brown/yellow, indicating that extractives were removed from the specimens. Recall that extractives can contaminate liquids, therefore changing their surface tension and altering wetting. It was possible then that water-saturation increased the surface polar extractive concentration (as evidenced by improved water wetting and impaired methylene iodide wetting). From Table 3-3, spotted gum and Gympie messmate contained similar amounts of water-soluble extractives; however, the impact of saturation was different for the two woods.

Polar groups on the wood surface may reorient in a fashion that could improve wetting. If this occurred, polar liquid wetting would become more favorable while nonpolar liquid wetting would become less favorable, as was observed in this study.

Because water saturation had a significant impact on liquid wetting, one naturally wonders if this observation might have some practical implications for the industry. For example, after veneer drying, instead of complete water saturation perhaps a light water spray on veneer surfaces could improve adhesive wetting and consequently bonding. If the effects of water saturation are explained by reorientation of wood surface molecules, then a simple surface water spray could be very beneficial. Furthermore, such applications of water are commonly employed as a surface pretreatment for use with moisture-cure polyurethane adhesives. However, if the effects of saturation are explained by a large-scale movement of extractives from within the bulk to the surface, then a simple water spray may not be useful. Consequently, a future research recommendation would be to determine if a simple water spray (prior to adhesive application) could improve bonding. It follows that the effects of pH, as well as various organic solvents that are water miscible (e.g. ethanol) should be included in such a study. Additionally, the time period between surface liquid spray and subsequent adhesive application could also be
important. Given the simplicity of a water spray prior to adhesive application and the potential significance to the industry, it seems that a deeper study of this concept would be valuable.

3.4.5. **Summary.**

Heating from a dry state showed that both spotted gum and Gympie messmate exhibited some sensitivity to thermal deactivation. However, the resulting changes were considered relatively minor. Heating from a dry state also revealed that Gympie messmate exhibited less-favorable wetting and greater sensitivity to thermal deactivation in comparison to spotted gum, exactly opposite of the expectation. Following the most-severe heating, polar liquid wetting was substantially reduced, indicating that both species became highly hydrophobic and thermally deactivated.

Initial contact angles were found to be misleading (showing no or slight wood sensitivity to heating), while time-dependent wetting was more informative (showing a greater wood sensitivity to heating). Time-dependent wetting was quantified with the wetting model K-value, but it was shown that consideration of the K-value alone could be misleading.

Water-saturation revealed clear differences in water permeability between woods (of the same growth conditions). Since wood permeability has implications for drying and adhesive penetration, further analysis of the permeability of these two species could be useful.

Finally, a method was developed to heat wood from a water-saturated state (to allow for movement of extractives during drying). This saturation process resulted in a notable observation. Water-saturation (followed by vacuum drying at room temperature) substantially altered the surface chemistry of both spotted gum and Gympie messmate. The surfaces of both woods became more hydrophilic following saturation which significantly improved water wetting. The changes, however, were more dramatic in Gympie messmate. This observation raised the question of whether a simple water-spray treatment onto the wood surface prior to adhesive application could be used to improve adhesive wetting and consequently bonding. If so, such treatment would be feasible to implement on the industrial scale and could prove very beneficial for manufacturers of wood composites. Further research of this observation is needed and should additionally include a study of the effects of pH, various water soluble organic solvents, and the time period between surface spray and subsequent adhesive application.
4 Results and Discussion: Sensitivity to Thermal Deactivation

4.1 Non-plantation Wood Sensitivity to Thermal Deactivation.
Non-plantation spotted gum and Gympie messmate were heated from a water-saturated state (MC > FSP). The non-plantation wood sensitivity to thermal deactivation was examined using initial contact angles and time-dependent wetting. Recall that it is generally expected for wood surface energy to decrease as wood surface temperature increases due to heating. In other words, we might expect the water initial contact angle will increase and the K-value will decrease as the heating severity increases (wood surface temperature increases). In contrast, we might expect a nonpolar liquid (e.g. methylene iodide) to exhibit reversed trends or at least a trend quite different from that of water.

4.1.1 Initial Contact Angles.
Initial contact angles were measured for the three liquids at each heat-treatment (surface temperature). Two things were noteworthy in Figure 4-1a,b. First, both woods often exhibited extreme variations in the observed water and formamide initial contact angles. Second, the initial contact angles did not exhibit the expected trends with respect to wood surface temperature (i.e. increase in initial contact angle due to increase in wood surface temperature). Instead, a highly erratic relationship was observed between surface temperature and initial contact angle. Since no clear relationship was apparent and given the relatively few number of experimental observations (S~2-3; n~4-5), no statistical analysis of this data was pursued. However, the data suggested that for most heat treatments, water and formamide initial contact angles were lower for Gympie messmate than for spotted gum.

Contrary to polar liquids (water and formamide), methylene iodide initial contact angles were approximately the same for both unheated woods (Figure 4-2). Although an erratic relationship was again observed between surface temperature and initial contact angle, heating to the highest
surface temperature (192°C) caused the methylene iodide initial contact angles to decrease on both woods.

**Figure 4-2**: Initial methylene iodide contact angles on non-plantation spotted gum and Gympie messmate as a function of surface temperature (ºC) during 200°C heating. Error bars represent ± 1 standard deviation.

### 4.1.2. Time-dependent Wetting.

Time-dependent wetting (quantified with K-value) was determined for each liquid at each heat-treatment. Recall, a large K-value refers to more-favorable, improved wetting while a small K-value refers to less-favorable, impaired wetting.

#### 4.1.2.1. Polar Liquid Time-dependent Wetting.

Water time-dependent wetting was more favorable on unheated Gympie messmate than unheated spotted gum (i.e. larger reduction in contact angle over time [Figure 4-3a,b] and larger K-value [Figure 4-4]). Examining the effects of heating, water time-dependent wetting was most favorable on unheated specimens (for both woods) and became less favorable as surface temp increased, in agreement with the general expectation. Upon heating to the highest surface temperature (192°C), both woods became thermally deactivated and highly hydrophobic.

Increasing heating, however, did not cause the expected gradual, continuous decrease in water time-dependent wetting. The 105°C data for both woods did not follow the expected trend (Figure 4-3a,b) and a discontinuity was seen in the corresponding K-value plot for both woods (Figure 4-4). This complexity (the apparent reversal in wetting trends) was unexpected. If it is real, then this discontinuity reflects an interesting change in surface character that might indicate changes in extractives concentration and/or reorientation of surface molecules. However, this discontinuity might be due to experimental error, or it might be an anomaly arising from the relatively low number of experimental observations (S~2; n~4). The two specimens were heat-treated to 105°C separately, so it was unlikely an error occurred during heating. Since non-plantation species were not separated according to heartwood region, sampling effects may have contributed to this discontinuity (it will be shown later that heartwood region impacts contact angle). Notice, however, that the discontinuity occurred for both woods at the same temperature.
This suggested that the discontinuity reflected a real surface phenomenon given the unlikelihood that experimental errors or anomalies would occur for both woods at the same temperature.

Note that for Gympie messmate heated to 130 and 165°C (Figure 4-3b) a sharp discontinuity appeared as a contact angle increase. This was an artifact from missing data when image acquisition started prematurely and occurred occasionally with the growing drop technique. However, this problem was eliminated with the static drop technique used to sample plantation woods.

![Graph showing water time-dependent wetting on non-plantation spotted gum (left) and Gympie messmate (right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.](image)

**Figure 4-3:** Water time-dependent wetting on non-plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.

![Graph showing water K-value on non-plantation spotted gum and Gympie messmate as a function of surface temperature (°C) during 200°C heating.](image)

**Figure 4-4:** Water K-value on non-plantation spotted gum and Gympie messmate as a function of surface temperature (°C) during 200°C heating.

Formamide time-dependent wetting was more favorable on unheated Gympie messmate than on unheated spotted gum (Figure 4-5a,b; 4-6). Note that formamide completely wetted unheated Gympie messmate (a datum point of 0.1° was manually inserted at 10 sec to signify complete wetting and to facilitate K-value curve fitting).
Like the results obtained with water, formamide time-dependent wetting was most favorable on unheated specimens and became less favorable as surface temperature increased. Upon heating to 192°C, both woods became thermally deactivated and highly hydrophobic. However, as seen with water, heating did not cause a gradual, continuous decrease in formamide time-dependent wetting. For both woods, the 130°C curve did not follow the expected trend (Figure 4-5a,b) and a discontinuity was seen in the corresponding K-value plot (Figure 4-6). This discontinuity again occurred at the same temperature for both woods but was more noticeable in Gympie messmate (recall a similar anomaly occurred with water [Figure 4-4]). As previously stated, this discontinuity appeared to reflect an actual and remarkable surface change since it occurred at the same temperature for both woods.

**Figure 4-5:** Formamide time-dependent wetting on non-plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (ºC) during 200°C heating. Error bars represent ± 1 standard deviation.

**Figure 4-6:** Formamide K-value on non-plantation spotted gum and Gympie messmate as a function of surface temperature (ºC) during 200°C heating.
4.1.2.2. Nonpolar Liquid Time-dependent Wetting.
Methylene iodide time-dependent wetting was more favorable on unheated spotted gum than unheated Gympie messmate (Figure 4-7a,b; 4-8). Notice that wetting trends for methylene iodide were reversed when compared to water and formamide. As surface temperature increased, methylene iodide time-dependent wetting tended to improve (Figure 4-8). This was particularly evident for spotted gum where the corresponding K-value plot showed a continuous increase in wetting as surface temperature increased. This behavior suggested that spotted gum became increasingly hydrophobic due to heating, consistent with the water and formamide observations. Gympie messmate also tended to become increasingly hydrophobic due to heating, but some complexity (two K-value discontinuities) was observed.

Careful inspection of Figures 4-4, 4-6, and 4-8 (the K-value plots for water, formamide, and methylene iodide, respectively) revealed that both woods exhibited discontinuities at the same temperature; however, the temperatures at which discontinuities occurred were different for the respective liquids. This peculiar observation strongly suggested that the K-value discontinuities (reversals in wetting trends) probably reflected real surface phenomena associated with notable changes in the two woods.

Figure 4-7: Methylene iodide time-dependent wetting on non-plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.
Figure 4-8: Methylene iodide K-value on non-plantation spotted gum and Gympie messmate as a function of surface temperature (ºC) during 200°C heating.

4.2. Plantation Wood Sensitivity to Thermal Deactivation.

Plantation wood sensitivity to thermal deactivation was examined using initial contact angles, time-dependent wetting, and also calculated surface energies.

4.2.1. Initial Contact Angles.

Initial contact angles were measured for the three liquids at each heat-treatment (surface temperature). Unlike with non-plantation woods, plantation woods did not exhibit extreme variations in observed initial contact angles, and trends generally aligned with the expectations. Therefore, a one-way ANOVA test with Tukey test means comparison (α=0.05) was conducted to compare effects of heating for each wood type. Complete statistical results are presented in Appendix C.

Water and formamide wetted Gympie messmate more favorably (lower contact angles) than spotted gum in nearly every instance of surface temperature (Figure 4-9a,b). For both woods, water and formamide initial contact angles were lowest on unheated specimens and tended to increase as surface temperature increased. The exception was formamide contact angle on Gympie messmate heated to 98ºC, which produced a significantly lower initial contact angle (p-value: 0.00) than unheated Gympie messmate.

Initial contact angles also revealed differences in the two wood’s sensitivity to thermal deactivation. Spotted gum was thermally deactivated at lower surface temperatures than Gympie messmate. Heating spotted gum to 105ºC (directly after evaporative cooling) significantly increased water initial contact angles (p-value: 0.00), while additional heating (from 105ºC) to 130, 165, and 192ºC did not significantly change water initial contact angles (p-value: 0.94, 0.81, and 0.90, respectively). In contrast, heating Gympie messmate to 105ºC did not significantly change water initial contact angles (p-value: 0.92), while additional heating (from 105ºC) to 165 and 192ºC significantly increased water initial contact angles (p-value: 0.00 and 0.00, respectively).

Similar statistical trends (to that of water) were observed using formamide (Appendix C).
Contrary to polar liquids (water and formamide), methylene iodide initial contact angles were approximately the same for both unheated woods and decreased due to heating (Figure 4-10). Initial contact angles again revealed differences in the two wood’s sensitivity to thermal deactivation at low surface temperatures. Heating to 105°C (directly after evaporative cooling) significantly decreased methylene iodide initial contact angles on both spotted gum and Gympie messmate (p-value: 0.00 and 0.01, respectively). However, the decrease in methylene iodide initial contact angles (from unheated to 105°C heated specimens) was greater on spotted gum (18%) than Gympie messmate (9%), suggesting again that spotted gum was more sensitive to thermal deactivation at low surface temperatures.
4.2.2. **Time-dependent Wetting.**

Time-dependent wetting was determined for each liquid at each heat-treatment and was quantified using the wetting model K-value.

4.2.2.1. **Polar Liquid Time-dependent Wetting.**

Water time-dependent wetting was more favorable on unheated Gympie messmate than unheated spotted gum (i.e. larger reduction in contact angle over time [Figure 4-11a,b] and larger K-value [Figure 4-12]). For both woods, wetting was most favorable on unheated specimens and became progressively worse as surface temperature increased. Upon heating to the highest surface temperature (192°C), both woods became thermally deactivated and highly hydrophobic.

As observed with the initial contact angles, the occurrence of thermal deactivation occurred at different surface temperatures for the two woods. After evaporative cooling (105°C), spotted gum became largely deactivated (water contact angles during time-dependent wetting were mostly greater than 90 degrees). In contrast, Gympie messmate continued to exhibit favorable wetting after evaporative cooling. This observation revealed that spotted gum is remarkably sensitive to thermal deactivation. Consequently, it appears that conventional kiln drying procedures could not produce good bonding surfaces for spotted gum.

Unlike observations with non-plantation woods, both plantation woods exhibited a simple continuous reduction in K-value as surface temperature increased (Figure 4-12).

---

**Figure 4-11:** Water time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.
Formamide time-dependent wetting trends were similar to that of water. Considering unheated specimens, Gympie messmate exhibited more-favorable wetting than spotted gum (Figure 4-13a,b). Note that formamide completely wetted Gympie messmate specimens heated to 130°C and lower temperatures. Examining heating effects, for both woods wetting was most favorable on unheated specimens and became progressively worse as surface temperature increased. Gympie messmate continued to exhibit favorable wetting as surface temperature increased. In contrast, heating caused spotted gum to become deactivated more readily than Gympie messmate.

Both woods showed a simple, continuous reduction in K-value as surface temperature increased (same as observed with water) (Figure 4-14). Notice, though, that at low surface temperatures, the K-values for Gympie messmate were substantially higher than spotted gum.

**Figure 4-12**: Water K-value on plantation spotted gum and Gympie messmate as a function of surface temperature (°C) during 200°C heating.

**Figure 4-13**: Formamide time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.
4.2.2.2. Nonpolar Time-dependent Wetting.

Trends observed with methylene iodide were opposite that observed for water and formamide. For unheated specimens, methylene iodide time-dependent wetting was similar for the two woods and, interestingly, became more favorable as surface temperature increased (Figure 4-15a,b). Methylene iodide wetting became substantially more favorable on spotted gum after heating which indicated that spotted gum became highly hydrophobic due to heating, much more so than Gympie messmate. Gympie messmate K-value essentially remained unchanged (Figure 4-16), suggesting that the wood was unchanged by heating; however a clear decrease in methylene iodide initial and equilibrium contact angle (Figure 4-15b) was observed. This is another example of how K-values alone can be misleading. In contrast, spotted gum K-value increased with increasing surface temperature (agreeing with the time-dependent wetting); however, the K-values exhibited a minor complexity (Figure 4-16).
Figure 4-15: Methylene iodide time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (ºC) during 200°C heating. Error bars represent ± 1 standard deviation.

Figure 4-16: Methylene iodide K-value on plantation spotted gum and Gympie messmate as a function of surface temperature (ºC) during 200°C heating.

4.2.3. Surface Energy Calculations.
Young’s equation assumes that the solid surface is ideally smooth, homogenous, undeformable, and in equilibrium with other phases (Johnson and Dettre, 1993). Wood, however, presents several complications to these assumptions, such as porosity, heterogeneity, and mass transfer of extractives into the liquid, changing liquid surface tension (Liptakova et al., 1998). These complications impact the contact angle time-dependency and consequently surface energy calculation. In this study, surface energies were calculated using contact angles from two acquisition times (0.1 and 10 sec, which represent initial and equilibrium contact angles, respectively).
Liquid surface tension components used to calculate surface energy are listed (Table 4-1).

<table>
<thead>
<tr>
<th>Liquids</th>
<th>$\gamma_L$</th>
<th>$\gamma_{LW}^L$</th>
<th>$\gamma_{AB}^L$</th>
<th>$\gamma_A^L$</th>
<th>$\gamma_B^L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.0</td>
<td>39.0</td>
<td>19.0</td>
<td>2.3</td>
<td>39.6</td>
</tr>
<tr>
<td>Methylene Iodide</td>
<td>50.8</td>
<td>50.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Wood surface energy ($\gamma_S$) and components, dispersive ($\gamma_{SW}^L$), polar ($\gamma_{AB}^S$), acidic ($\gamma_A^S$), and basic ($\gamma_B^S$), were determined for both woods at each heat-treatment.

### 4.2.3.1. Negative Contributions to Surface Energy.

The acid-base theory has been known to occasionally produce negative square roots ($\sqrt{\gamma_B^S}$ and $\sqrt{\gamma_A^S}$) with certain contact angle data. If only one square root is negative, the total acid-base component is negative, which leads to a negative contribution to total surface energy (Meijer et al., 2000). A negative $\gamma_{AB}^S$ could be allowed in a mechanically stable condensed phase, provided that the total surface energy is still positive (Good and van Oss, 1992). The reason for and meaning of negative square roots, though, is not fully understood (Volpe and Siboni, 2000).

Good (1992) found that the negative $\sqrt{\gamma_B^S}$ occurred only rarely and when experimental error may be the cause. Meijer et al. (2000) observed that negative $\sqrt{\gamma_B^S}$ values occurred during very high water contact angles. Negative $\sqrt{\gamma_A^S}$ occurred more often; however, no definite explanation was given as to their meaning (Good, 1992).

Some consider the negative values to be artifacts and that they should be corrected to zero. Volpe and Siboni (1997) stated that standard deviations of negative numbers are often larger than the coefficients themselves and therefore the value may be zero. Michalski et al. (1998) suggested that small negative values (< 0.05 mJ/m$^2$) could essentially be zero. However, Mohammed-Ziegler et al. (2004) found negative square root values to be as large as 7.3 mJ/m$^2$.

If the negative square root is an artifact caused by an inaccurate contact angle measurement, then simply “adjusting” the contact angle value would result in a positive value (Good and van Oss, 1992). However, often a large “correction” (approximately 20°) in the contact angle value is needed to bring the acid component value from -0.5 into the positive range (Good and van Oss, 1992; Michalski et al., 1998). In many cases, the need for such a large correction in contact angle is not likely caused by an inaccurate measurement. However, on porous, heterogeneous materials (where liquid sorption and contamination may occur) a large change in contact angle is observed over time (Good and van Oss, 1992).

Some propose that negative values are empirically valid (Good and van Oss, 1992). Good (1992) and Meijer et al. (2000) suggested that the negative $\sqrt{\gamma_A^S}$ are physically real and caused...
by an acid character in the surface leading to a negative contribution to the total solid surface energy. Michalski et al. (1998) found that negative square roots occurred regardless of the liquid triplet that was used. However, use of more than the minimum (three) liquids helped overcome sensitivities to erratic and negative results (Shalel-Levanon and Marmur, 2003; Volpe and Siboni, 1997). Ultimately, though, the acid-base theory formulism appeared to be considered responsible for the occurrence of negative square roots (Greiveldinger and Shanahan, 1999; Shalel-Levanon and Marmur, 2003). This led some to suggest that the theory is inadequate for a broad range of surfaces (Greiveldinger and Shanahan, 1999) and certainly inadequate for the detailed analysis of a complex system such as wood (Mohammed-Ziegler et al., 2004).

Nevertheless, the acid-base theory was used in this study. Woodward (2000) stated that the negative values were not of consequence when the relative values (e.g. of two species) were considered. Negative values were obtained and, following examples of Mohammed-Ziegler et al. (2004) and Meijer et al. (2000), where reported as such.

**4.2.3.2. Surface Energy: Initial Contact Angles.**

Surface energies calculated with initial contact angles were determined for spotted gum (Table 4-2) and Gympie messmate (Table 4-3).

Comparing the unheated specimens, Gympie messmate surface energy was higher than spotted gum. Heating, however, increased the surface energy for both woods. This is clearly wrong when considering the time-dependent wetting behavior of water in this study. In addition, literature has shown that thermal deactivation decreases wood’s surface energy (Gerardin et al., 2007). Again, it seems that initial contact angles and the surface energies calculated with them are potentially misleading and perhaps of little practical value.

Anomalous results were also obtained. Negative acid components were calculated for spotted gum on all surface temperatures and for Gympie messmate heated to 192ºC. It was observed that negative acid components occurred during high (> 80º) formamide contact angles. Negative base components were calculated for Gympie messmate heated to 165 and 192ºC and occurred during high (> 110º) water contact angles (agreeing with Meijer et al. [2000]). However, comparatively high water contact angles did not produce negative base components for spotted gum.

**Table 4-2:** Initial Contact Angles, Avg. and (Std dev), and corresponding Surface Energies for Spotted Gum.

<table>
<thead>
<tr>
<th>Surface Temp. (°C)</th>
<th>Contact Angle (deg)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>HCONH₂</td>
</tr>
<tr>
<td>25</td>
<td>94.4 (11.3)</td>
<td>84.8 (10.8)</td>
</tr>
<tr>
<td>98</td>
<td>103.7 (15.7)</td>
<td>83.6 (10.6)</td>
</tr>
<tr>
<td>105</td>
<td>109.5 (12.5)</td>
<td>87.0 (11.4)</td>
</tr>
<tr>
<td>130</td>
<td>112.0 (10.4)</td>
<td>87.4 (9.5)</td>
</tr>
<tr>
<td>165</td>
<td>113.0 (11.6)</td>
<td>91.8 (8.6)</td>
</tr>
<tr>
<td>192</td>
<td>112.4 (8.0)</td>
<td>93.7 (5.0)</td>
</tr>
</tbody>
</table>
Table 4-3: Initial Contact Angles, Avg. and (Std dev), and corresponding Surface Energies for Gympie Messmate.

<table>
<thead>
<tr>
<th>Surface Temp. (ºC)</th>
<th>Contact Angle (deg)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>HCONH₂</td>
</tr>
<tr>
<td>25</td>
<td>90.2 (10.2)</td>
<td>70.0 (10.9)</td>
</tr>
<tr>
<td>98</td>
<td>85.8 (11.7)</td>
<td>57.7 (9.9)</td>
</tr>
<tr>
<td>105</td>
<td>92.5 (10.0)</td>
<td>63.8 (16.6)</td>
</tr>
<tr>
<td>130</td>
<td>98.7 (8.5)</td>
<td>65.3 (10.9)</td>
</tr>
<tr>
<td>165</td>
<td>110.7 (7.2)</td>
<td>72.1 (12.7)</td>
</tr>
<tr>
<td>192</td>
<td>117.9 (5.8)</td>
<td>87.1 (6.3)</td>
</tr>
</tbody>
</table>

4.2.3.3. Surface Energy: Equilibrium Contact Angles.

Surface energies measured with equilibrium contact angles were determined for spotted gum (Table 4-4) and Gympie messmate (Table 4-5).

Comparing the unheated specimens, Gympie messmate surface energy was higher than spotted gum. Unlike surface energy calculated with initial contact angles, equilibrium contact angle surface energies resulted in more sensible trends and also revealed differences in the two wood’s sensitivity to thermal deactivation. Spotted gum surface energy decreased rapidly upon heating to 105ºC, while Gympie messmate surface energy did not decrease as substantially until heated to approximately 165ºC. This demonstrated that at lower surface temperatures, spotted gum was more thermally deactivated than Gympie messmate.

Differences between the two woods were also observed in the energy components. In spotted gum, the dispersive component comprised the majority of surface energy at all surface temperatures. In contrast, the base component comprised the majority of Gympie messmate surface energy at 25 and 98ºC surface temperatures, after which the dispersive component comprised the majority. This agreed with methylene iodide time-dependent wetting in this study which showed spotted gum was more hydrophobic than Gympie messmate.

Anomalous results were also obtained. Negative base components were calculated for both woods at higher surface temperatures but no acid components were calculated. It was observed that negative base components occurred during high (> 85º) water contact angles (agreeing with Meijer et al. [2000]).
### Table 4-4: Equilibrium Contact Angles, Avg. and (Std dev), and corresponding Surface Energies for Spotted Gum.

<table>
<thead>
<tr>
<th>Surface Temp. (ºC)</th>
<th>Contact Angle (deg)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>HCONH₂</td>
</tr>
<tr>
<td>25</td>
<td>44.8 (17.7)</td>
<td>6.6 (4.9)</td>
</tr>
<tr>
<td>98</td>
<td>72.8 (21.1)</td>
<td>12.3 (9.4)</td>
</tr>
<tr>
<td>105</td>
<td>86.4 (18.6)</td>
<td>20.2 (14.0)</td>
</tr>
<tr>
<td>130</td>
<td>95.6 (14.0)</td>
<td>27.8 (14.4)</td>
</tr>
<tr>
<td>165</td>
<td>104.1 (16.9)</td>
<td>46.3 (14.4)</td>
</tr>
<tr>
<td>192</td>
<td>108.4 (8.1)</td>
<td>68.0 (7.0)</td>
</tr>
</tbody>
</table>

### Table 4-5: Equilibrium Contact Angles, Avg. and (Std dev), and corresponding Surface Energies for Gympie Messmate.

<table>
<thead>
<tr>
<th>Surface Temp. (ºC)</th>
<th>Contact Angle (deg)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>HCONH₂</td>
</tr>
<tr>
<td>25</td>
<td>23.5 (4.9)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>98</td>
<td>26.4 (7.7)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>105</td>
<td>37.7 (14.5)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>130</td>
<td>56.4 (18.0)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>165</td>
<td>95.2 (11.5)</td>
<td>10.8 (7.8)</td>
</tr>
<tr>
<td>192</td>
<td>114.8 (7.7)</td>
<td>57.9 (8.9)</td>
</tr>
</tbody>
</table>

### 4.2.3.3.1. Comparison to Literature.

Surface energy measured with equilibrium contact angles was within the range (43-58 mJ/m²) of unheated tropical species also measured with equilibrium contact angles (Table 4-6) (Mohammed-Ziegler et al., 2004). Compared to these tropical species (Mohammed-Ziegler et al., 2004), spotted gum and Gympie messmate exhibited smaller dispersive components. Acid and base components, though, were larger than most tropical species (Mohammed-Ziegler et al., 2004). This could have been caused by the spotted gum and Gympie messmate water-saturation process (recall that water-saturation resulted in more-favorable water wetting and less-favorable methylene iodide wetting).
Table 4-6: Comparison of Various Wood Surface Energies Calculated with Equilibrium Contact Angles.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\gamma_S$</th>
<th>$\gamma_S^{LW}$</th>
<th>$\gamma_S^A$</th>
<th>$\gamma_S^B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>spotted gum</td>
<td>56.05</td>
<td>37.38</td>
<td>3.99</td>
<td>21.83</td>
</tr>
<tr>
<td>Gympie messmate</td>
<td>58.03</td>
<td>37.65</td>
<td>2.38</td>
<td>43.58</td>
</tr>
<tr>
<td>Almond a</td>
<td>54.6</td>
<td>47.6</td>
<td>0.2</td>
<td>56.1</td>
</tr>
<tr>
<td>Cloves a</td>
<td>42.8</td>
<td>41.2</td>
<td>3.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Guava a</td>
<td>57.5</td>
<td>48.5</td>
<td>1.4</td>
<td>17.1</td>
</tr>
<tr>
<td>Mango a</td>
<td>58.1</td>
<td>48.3</td>
<td>1.2</td>
<td>20.1</td>
</tr>
<tr>
<td>Neem a</td>
<td>55.2</td>
<td>46.1</td>
<td>2.1</td>
<td>10.4</td>
</tr>
<tr>
<td>Teak a</td>
<td>50.3</td>
<td>42.6</td>
<td>0.2</td>
<td>59.3</td>
</tr>
</tbody>
</table>

a. Reference (Mohammed-Ziegler et al., 2004).

4.2.4. Discussion: Sensitivity to Thermal Deactivation.
Specimens were heated from a water-saturated state to allow for movement of extractives during drying. Both non-plantation and plantation woods were examined; however, this discussion will focus on plantation woods. Sensitivity to thermal deactivation was investigated using initial contact angles, time-dependent wetting, and surface energies measured with equilibrium contact angles (surface energy measured with initial contact angles did not follow the same trends and did not agree with literature). Considering the information obtained from initial contact angles and time-dependent wetting, this study indicated that the latter was much more informative and more consistent with the general expectations of wetting on wood surfaces. Time-dependent wetting was quantified using the wetting model K-value which allowed for determining effects of heat-treatments. However, observing the K-value alone could be misleading in some instances.

Comparing unheated wood, Gympie messmate wetted more favorably than spotted gum. Heating revealed differences in the two wood’s sensitivity to thermal deactivation. Spotted gum was remarkably more susceptible to thermal deactivation at low temperatures (i.e. mild drying temperatures after evaporative cooling) in comparison to Gympie messmate. Substantial wood drying does not occur until temperatures above that required for evaporative cooling. Consequently, in order to dry spotted gum using conventional kiln drying operations, its surface temperature must be raised to a temperature that impairs adhesion. Gympie messmate, however, appears amenable to more typical drying conditions used in the industry.

In this study, both woods became thermally deactivated and highly hydrophobic upon heating to the highest surface temperature (192ºC). The mechanism by which the woods became deactivated was unknown; however, in the literature Christiansen (1990; 1991) discussed chemical and physical mechanisms by which high-temperature drying could result in wood thermal deactivation that was observed in this study. These include: irreversible micropore closure in the cell wall, reorientation of surface molecules, oxidation and pyrolysis of bonding sites, and extractives movement to the surface (Christiansen, 1990; 1991).
Wood micropore closure during drying reduces liquid penetration (Christiansen, 1990). Since liquid penetration causes a decrease in contact angle over time (Liptakova and Kudela, 1994), micropore closure was expected to cause wetting to become less favorable. However, Fengel and Wegner (1984) discussed cracks occurring in the middle lamella and S1 layers of spruce wood heated between 180 – 200ºC. Production of cracks was expected to cause wetting to become more favorable. In this study, following heating, polar liquid wetting became less favorable but nonpolar liquid wetting became more favorable, suggesting that thermal deactivation was not limited to changes in the surface structure alone.

During drying, polar surface molecules reorient inwards (away from the wood-air interface and towards the bulk material) resulting in a higher concentration of hydrocarbons on the surface and consequently a more hydrophobic surface (Christiansen, 1990). This effect was accelerated at high temperatures and moisture content when lignin and hemicellulose were above their respective glass transition temperatures (Christiansen, 1990).

Hemicelluloses are able to form hydrogen bonds with water molecules and consequently, hemicellulose degradation leads to a reduction in wood’s affinity for water (Gerardin et al., 2007). It does not appear, though, that treatment temperatures used in this study were capable of causing substantial hemicellulose degradation, since hemicellulose degradation occurs between 220 – 315ºC (Yang et al., 2007). Heating also causes an increase in surface lignin content. Lignin is a hydrophobic material, and consequently, an increase in concentration on the wood surface causes less-favorable polar liquid wetting yet more-favorable nonpolar liquid wetting (Sernek, 2002). However, an increase in lignin content is due to hemicellulose degradation, which as previously explained may not have occurred.

Extractives present on the wood surface are regarded as the principal cause of surface deactivation (Vick, 1999). Nonpolar extractives can move to the wood’s surface during high-temperature drying (Hse and Kuo, 1988) and lower wood surface polarity, consequently reducing polar liquid wetting (Widsten et al., 2006; Chen, 1970). Additionally, it was possible that nonpolar extractives could also be moved to the wood surface either through steam distillation or as surface active contaminants in liquid water when wood is heated from a water-saturated state. Following heating, polar liquid (water and formamide) wetting became less favorable, while nonpolar liquid (methylenedioide) wetting became more favorable. Widsten et al. (2006) found that spotted gum contained 6.5% phenolic and 3.08% lipophilic extractives. No comparative data for Gympie messmate was obtained; however, six other Eucalypt species exhibited a range of 0.6 – 6.8% phenolic and 0.09 – 0.54% lipophilic extractives (Widsten et al., 2006). It was likely, then, that spotted gum contained a higher percentage of nonpolar extractives, which helps explain spotted gum’s more hydrophobic surface in comparison to Gympie messmate.

Successfully bonding spotted gum likely requires careful adhesive formulation. Time-dependent wetting (quantified with the K-value) of polar and nonpolar liquids provides an early indicator of how water- or oil-based adhesives might perform. Polar liquid (water and formamide) wetting became less favorable following heating; however, formamide wetted both woods more favorably than water at comparable surface temperatures. This was expected since water has a
higher surface tension (72.8 mJ/m²) than formamide (58.0 mJ/m²). According to Young’s equation, the contact angle and interfacial energies are related through:

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]  

(4-1)

where \(\gamma_{SV}\), \(\gamma_{SL}\), and \(\gamma_{LV}\) are the interfacial energies of the solid/vapor, solid/liquid, and liquid/vapor, respectively. A high solid surface energy or a low liquid surface tension will form a low contact angle. At each treatment, the solid (i.e. wood) surface was fixed, so a lower contact angle represented a liquid with lower surface tension. Consequently, reducing an adhesive’s surface tension (by applying a wetting agent or surfactant) will result in more-favorable wetting on the highly hydrophobic and thermally sensitive spotted gum surface.

Additionally, spotted gum’s highly hydrophobic surface suggested using a non-aqueous adhesive (e.g. a polyurethane) to improve adhesive wetting and bonding performance, although McGavin et al. (2013) reported poor results with such a strategy. Recall that nonpolar liquid (methylene iodide) time-dependent wetting interestingly improved following heating for spotted gum. Further research is necessary to see if the observed improvement in nonpolar liquid wetting actually results in improved bonding with a nonpolar adhesive.

In summary, spotted gum was shown to be remarkably sensitive to thermal deactivation. Heating spotted gum to a surface temperature of only 105°C resulted in water contact angles that exceeded 90° even after 10 seconds of wood/liquid contact. If this were the case for a water-based adhesive, then adhesive penetration would not occur through capillary forces but only through compaction forces during bondline consolidation. Such conditions will contribute to air entrapment within the bondline which may lead to damaging stress concentrations. Consequently, according to the observations in this study, it appears that conventional kiln drying procedures will always result in poor (i.e. thermally deactivated) spotted gum surfaces. This suggests that significant economic barriers could prevent the industrial use of spotted gum in the wood composites industry. Since drying methods are unlikely to change in the near future, spotted gum likely requires novel strategies to improve adhesive wetting. Considering that McGavin et al. (2013) found that phenol-formaldehyde adhesives were the most promising in comparison to melamine-urea and polyurethane adhesives, it seems that phenol-formaldehyde resoles should be considered in combination with a variety of surface active wetting agents.

4.3. Heartwood Sub-sampling and Sensitivity to Thermal Deactivation.

Up to this point, all specimens were classified as occurring in the heartwood region, with no additional qualification. However, plantation wood specimens were sub-sampled with respect to three heartwood regions, referred to as inner, middle, and outer heartwood. The sub-sampled regions were defined by specimen dimensions taken from the heartwood region; they were not specified by the number of growth increments within the heartwood.

Spotted gum and Gympie messmate heartwood region’s sensitivity to thermal deactivation was examined using water and methylene iodide time-dependent wetting (with K-values) and equilibrium contact angles. Three surface temperatures were examined: unheated (control),
105°C, and 192°C. In this discussion, comparisons were made between inner and outer heartwood, since middle heartwood generally trends with one or the other.

4.3.1. Water Time-dependent Wetting.
Examining the unheated spotted gum, water time-dependent wetting was more favorable on outer heartwood than inner heartwood (Figure 4-17a) which corresponded to a larger outer heartwood water K-value (Figure 4-20a). Similarly, examining the unheated Gympie messmate, water time-dependent wetting was slightly more favorable on outer heartwood than inner heartwood (Figure 4-17b; Figure 4-20b). Differences in heartwood region wettability, though, were less obvious in Gympie messmate than in spotted gum.

**Figure 4-17:** Water time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) heartwood regions, unheated. Error bars represent ± 1 standard deviation.

Similar trends were observed upon heating to 105°C surface temperature. Water time-dependent wetting was again more favorable on outer spotted gum heartwood than inner heartwood (Figure 4-18a; Figure 4-20a). In contrast, no clear differences were detected between Gympie messmate outer and inner heartwood (Figure 4-18b; Figure 4-20b).

**Figure 4-18:** Water time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) heartwood regions heated to 105°C. Error bars represent ± 1 standard deviation.
Upon heating to 192°C, both woods showed that water time-dependent wetting was more favorable on outer heartwood than inner heartwood (Figure 4-19a,b), but differences were more noticeable in spotted gum. No differences were observed in the corresponding water K-values for both woods (Figure 4-20a,b). This again suggested that K-values alone could be misleading.

**Figure 4-19:** Water time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) heartwood regions heated to 192°C. Error bars represent ± 1 standard deviation.

4.3.2. **Methylene Iodide Time-dependent Wetting.**
Examining both unheated woods, methylene iodide time-dependent wetting was less favorable on outer heartwood than inner heartwood (Figure 4-21a,b) but corresponding K-values showed little difference among the heartwood regions (Figure 4-24a,b).
Figure 4-21: Methylene iodide time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) heartwood region, unheated. Error bars represent ± 1 standard deviation.

Upon heating to 105°C surface temperature, spotted gum outer heartwood continued to wet less favorably than inner heartwood (Figure 4-22a), but this again was not observed in the corresponding K-values (Figure 4-24a). In contrast, no clear differences were detected between Gympie messmate heartwood regions (Figure 4-22b; 4-24b).

Figure 4-22: Methylene iodide time-dependent wetting on plantation spotted gum (a: left) and Gympie messmate (b: right) heartwood regions heated to 105°C. Error bars represent ± 1 standard deviation.

Similar trends were observed upon heating to 192°C. Again, methylene iodide time-dependent wetting was less favorable on spotted gum outer heartwood than inner heartwood (Figure 4-23a; 4-24a), while Gympie messmate showed little to no difference between heartwood regions (Figure 4-23b; 4-24b).
4.3.3. Equilibrium Contact Angles.

Water and methylene iodide equilibrium contact angles were compared for both woods using the three surface temperatures: unheated (control), 105°C, and 192°C. A two sample t-Test with Welch correction factor (α=0.05) was conducted comparing inner and outer heartwood at each surface temperature. Middle heartwood again was excluded from the statistical comparison since results were generally between inner and outer values.

Examining spotted gum, water equilibrium contact angles on outer heartwood were significantly lower than those on inner heartwood (p-value: 0.06, 0.02, and 0.03 for unheated, 105°C, and 192°C heated specimens, respectively) (Figure 4-25a). Note that for unheated spotted gum, the p-value (0.06) was greater than the alpha (0.05), but differences could be found to be significant upon further sampling.
In contrast, Gympie messmate exhibited no significant difference between outer and inner heartwood (p-value: 0.19, 0.53, and 0.14 for unheated, 105°C, and 192°C heated specimens, respectively) (Figure 4-25b).

Similar to results obtained with water, examining spotted gum showed that methylene iodide equilibrium contact angles were significantly higher on outer heartwood than those on inner heartwood (p-value: 0.00, 0.02, and 0.02 for unheated, 105°C, and 192°C heated specimens, respectively) (Figure 4-26a).

Examining Gympie messmate, methylene iodide equilibrium contact angles were possibly significantly different on unheated outer and inner heartwood (p-value: 0.08), but upon heating, no significant differences were detected (p-value: 0.94 and 0.79 for 105°C and 192°C heated specimens, respectively) (Figure 4-26b).
4.3.4. Discussion: Comparison of Heartwood Regions.
Significant differences between inner and outer heartwood regions were observed for spotted gum. Gympie messmate also exhibited slight differences between inner and outer heartwood, but these differences were not significant and were less than those observed in spotted gum. For both woods, water and methylene iodide wetting revealed that outer heartwood was more hydrophilic than inner heartwood. This may be due to differences in extractive concentration in various heartwood regions. Examining several Eucalyptus species, Wilkes (1984) found that the outer heartwood contained more polar (water- and methanol-soluble) extractives than inner heartwood. Polar extractives may contaminate liquids during contact angle measurements, therefore reducing the liquid’s surface tension and resulting in a larger change in contact angle over time.

Australian plantation spotted gum and Gympie messmate were compared to North American loblolly pine and Douglas-fir. Comparisons were made using water and methylene iodide time-dependent wetting (with K-values) and equilibrium contact angles. All woods were heat-treated from a water-saturated state and comparisons were made using three surface temperatures: unheated (control), 105°C, and 192°C. Plantation Australian wood (spotted gum and Gympie messmate) time-dependent wetting data was previously reported (section 4.2.2). Here, the same data is presented for direct comparison to North American wood loblolly pine and Douglas-fir.

4.4.1. Water Time-dependent Wetting.
Comparing unheated surfaces, water time-dependent wetting was more favorable on Gympie messmate and Douglas-fir than compared to spotted gum and loblolly pine (Figure 4-27a,b; 4-28a,b). For all woods, the unheated surfaces exhibited the most favorable water wetting which became progressively less favorable as surface temperature increased. However, the degree of thermal deactivation occurred at different surface temperatures for the woods. After evaporative cooling (105°C), both spotted gum and loblolly pine became thermally deactivated (water contact angle was mostly greater than 80 – 90 degrees during time-dependent wetting). In contrast, Gympie messmate and Douglas-fir continued to exhibit favorable wetting even after evaporative cooling. This observation was surprising since it indicated that spotted gum and loblolly pine were similarly sensitive to thermal deactivation, and yet loblolly pine is successfully bonded in the industry. This point will be revisited below when considering methylene iodide wetting.

All woods exhibited a simple continuous reduction in K-value as surface temperature increased (Figure 4-29a,b). Upon heating to the highest surface temperature (192°C), all woods became highly hydrophobic and similarly deactivated.
Figure 4-27: Water time-dependent wetting on spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.

Figure 4-28: Water time-dependent wetting on loblolly pine (a: left) and Douglas-fir (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.

Figure 4-29: Water K-value on North American woods (a: left) and Australian woods (b: right) as a function of surface temperature (°C) during 200°C heating.
4.4.2. Methylene Iodide Time-dependent Wetting.
Methylene iodide time-dependent wetting exhibited quite different trends in the North American woods than was expected. Comparing unheated specimens, methylene iodide time-dependent wetting was more favorable on loblolly pine and Douglas-fir than compared to spotted gum and Gympie messmate (Figure 4-30a,b; 4-31a,b). Increasing surface temperature resulted in a simple, continuous increase in K-value (i.e. wetting became more favorable) for spotted gum (Figure 4-32b). Gympie messmate, though, showed little to no change in K-value upon heating (Figure 4-32b). In contrast to the Australian woods, both loblolly pine and Douglas-fir exhibited complex K-value behavior upon heating. Loblolly pine K-value first increased and then decreased upon heating to 105°C and 192°C, respectively (Figure 4-32a). Douglas-fir K-value first decreased and then increased upon heating to 105°C and 192°C, respectively (Figure 4-32a). Douglas-fir exhibited significantly larger variability in time-dependent wetting than loblolly pine and the Australian woods.

Upon heating to the highest surface temperature (192°C), Douglas-fir exhibited the most hydrophobic surface (highest K-value) followed by spotted gum and loblolly pine K-values which were similar. Gympie messmate exhibited the least hydrophobic surface upon heating to 192°C.

Recall from above than spotted gum and loblolly pine appeared similarly sensitive to thermal deactivation when considering water wetting behavior. In the case of methylene iodide wetting however, it is apparent that spotted gum and loblolly pine are indeed quite different. On loblolly pine, heating does not substantially change methylene iodide wetting, which is in sharp contrast to spotted gum which exhibits a large increase in methylene iodide wetting due to heating. This is a good example of the complexity of wood surface chemistry, and for the need to observe surface effects using multiple liquids.

Figure 4-30: Methylene iodide time-dependent wetting on spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.
4.4.3. Equilibrium Contact Angles.

Water and methylene iodide equilibrium contact angles on North American and Australian woods were compared using three surface temperatures: unheated (control), 105°C, and 192°C. A one-way ANOVA test with Tukey test means comparison ($\alpha=0.05$) was conducted comparing effects of heating for each wood. Considering the methylene iodide data for North American woods, since no clear relationship was apparent, no statistical analysis of methylene iodide data was pursued.

Comparing the unheated woods, Douglas-fir and Gympie messmate exhibited the lowest water equilibrium contact angles while loblolly pine and spotted gum exhibited the highest (Figure 4-33a, b). This was expected since water time-dependent wetting was greatest on Douglas-fir and Gympie messmate (Figure 4-27b; 4-28b).
Heating caused the water equilibrium contact angle to increase on all woods (Figure 4-33a,b). This increase was significant upon heating from control (unheated) to 105°C (p-value: 0.00 for all woods) and upon additional heating from 105°C to 192°C (p-value: 0.00 for all woods). Following the highest surface temperature (192°C), water equilibrium contact angles were slightly higher on Australian woods than on North American woods, suggesting the Australian woods were more hydrophobic.

![Graph](image)

**Figure 4-33:** Water equilibrium contact angles on North American woods (a: left) and Australian woods (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.

As previously mentioned, methylene iodide equilibrium contact angles exhibited quite different trends in the North American woods than was expected. Comparing the unheated woods, North American woods exhibited the lowest methylene iodide equilibrium contact angles while Australian woods exhibited the highest (Figure 4-34a,b). This was expected since methylene iodide time-dependent wetting was greatest on North American woods (Figure 4-32a,b).

Heating caused the methylene iodide equilibrium contact angle to decrease on spotted gum and Gympie messmate (Figure 4-34b). However, heating did not produce consistent trends in the two North American woods (Figure 4-34a). Upon heating to the highest surface temperature (192°C), Gympie messmate exhibited the highest contact angle followed by spotted gum and loblolly pine which were similar. Methylene iodide completely wetted Douglas-fir.
In summary, the comparison of Australian and North American woods initially seemed somewhat surprising. Specifically, water wetting data suggested that spotted gum and loblolly pine were similarly sensitive to thermal deactivation. This seemed counterintuitive since loblolly pine is a major wood resource used in the North American wood composites industry, but spotted gum experiences poor adhesion properties. However, comparing spotted gum and loblolly pine using methylene iodide revealed large differences between the two woods. This study does not explain why bonding is successful in loblolly pine and not spotted gum but instead reveals, through methylene iodide wetting, that the respective woods are quite different. In the same fashion, water revealed that Gympie messmate and Douglas-fir were similarly sensitive to thermal deactivation, as both were less susceptible to thermal deactivation at low drying temperatures in comparison to spotted gum and loblolly pine. Again, though, clear differences were detected between the Gympie messmate and Douglas-fir when sampling with methylene iodide. These observations represent a good example of the complexity of wood surface chemistry, and for the need to observe surface effects using multiple liquids with different polarities.

**Figure 4-34:** Methylene iodide equilibrium contact angles on North American woods (a: left) and Australian woods (b: right) as a function of surface temperature (°C) during 200°C heating. Error bars represent ± 1 standard deviation.
5 Conclusions and Recommendations for Future Research

This research intended to compare and contrast the surface chemistries of Australian spotted gum and Gympie messmate with a particular focus on sensitivity to thermal deactivation. Both non-plantation and plantation Australian woods were examined. The plantation Australian woods were further studied to determine differences in surface chemistry across the heartwood. Finally, plantation spotted gum and Gympie messmate were compared to two commonly used North American woods, loblolly pine and Douglas-fir.

Wetting measurements using water, formamide, and methylene iodide were performed using the sessile drop method. Initial and equilibrium contact angles, time-dependent wetting, and surface energy (measured with initial and equilibrium contact angles) were determined. Considering the information obtained from initial contact angles and time-dependent wetting, this study indicated that the latter was much more informative and more consistent with the general expectations of wetting on deactivated wood surfaces. Time-dependent wetting was quantified using a parameter (K-value) from a curve fitting wetting model. However, in this study it was shown that observing the K-value alone could be misleading in some instances. Surface energy (calculated at both initial and equilibrium contact angles) occasionally resulted in anomalous (negative energy component) values. Additionally, surface energy calculated with initial contact angles did not follow trends specified in literature or agree with time-dependent wetting observations from this study.

Wood was heated from both dry and water-saturated states. Heating dry wood showed that both spotted gum and Gympie messmate exhibited some sensitivity to thermal deactivation. However, the resulting changes were considered relatively minor. Heating from a dry state also revealed that Gympie messmate exhibited less-favorable wetting and greater sensitivity to thermal deactivation in comparison to spotted gum, exactly opposite of the expectation. Consequently, a method was developed to heat wood from a water-saturated state to allow for the movement of extractives during drying and better represent industrial practices. Heating from a water-saturated state showed both spotted gum and Gympie messmate were more sensitive to thermal deactivation in comparison to heating from a dry state.

Heating from a water-saturated state revealed that spotted gum was remarkably more sensitive to thermal deactivation at low surface temperatures in comparison to Gympie messmate. Heating spotted gum to a surface temperature of only 105°C (directly after the stage of evaporative cooling) resulted in water contact angles that exceeded 90° even after 10 seconds following wood/liquid contact. If this wetting behavior occurred with water-based adhesives, then adhesive penetration would not occur through capillary forces but only as a result of compaction during bondline consolidation. Such conditions would contribute to air entrapment within the bondline which may lead to damaging stress concentrations within the composite product. Since spotted gum exhibited severe deactivation at low surface temperatures, it was suggested that conventional kiln drying operations may not be feasible for drying spotted gum. This suggests that significant economic barriers could prevent the industrial use of spotted gum in the wood composites industry. In contrast, Gympie messmate appears amenable to more typical drying conditions used in the industry.
Comparing the plantation wood’s various heartwood regions revealed that significant differences between inner and outer heartwood were observed for spotted gum. Gympie messmate also exhibited slight differences between inner and outer heartwood, but these differences were not significant and were less than those observed in spotted gum.

The comparison of Australian and North American woods seemed somewhat surprising. Water wetting revealed that spotted gum and loblolly pine were similarly sensitive to thermal deactivation (both were severely deactivated at low surface temperatures). This observation seemed counterintuitive since loblolly pine is used extensively in the North American composites industry while spotted gum experiences poor adhesion properties. However, methylene iodide wetting revealed large differences between spotted gum and loblolly pine. In the same fashion, water revealed that Gympie messmate and Douglas-fir were similarly sensitive to thermal deactivation, as both were less susceptible to thermal deactivation at low drying temperatures in comparison to spotted gum and loblolly pine. However, methylene iodide wetting behavior again revealed clear differences between Gympie messmate and Douglas-fir.

Three areas of future research were suggested:

1) Water-saturation (followed by vacuum drying at room temperature) substantially altered the surface chemistries of both spotted gum and Gympie messmate. The surfaces of both woods became more hydrophilic following saturation which significantly improved water wetting. Given the significant impact this had on wetting, the question was raised of whether a simple water-spray treatment (rather than complete saturation) onto the wood surface prior to adhesive application could improve bonding. If so, a simple surface spray could have practical and very beneficial implications for the industry and would be feasible to implement (seeing how similar such applications are commonly used as pretreatments for moisture-cure polyurethane adhesives). It is recommended that research regarding the surface spray treatment include a study on the effects of pH, the use of various water-soluble organic solvents, and the impact of time period between surface spray and subsequent adhesive application.

2) Water-saturation also revealed clear differences in water permeability between spotted gum and Gympie messmate. Wood permeability is known to effect adhesive penetration and wood drying, and consequently, further study of these two areas may help explain bonding differences between spotted gum and Gympie messmate.

3) In this study, results indicated that spotted gum became severely thermally deactivated at low drying temperatures. Since it is unlikely that conventional kiln drying operations will change in the near future, use of spotted gum in the wood composites industry may require adhesive formulations which exhibit reduced surface tensions. Deactivated spotted gum exhibited a highly hydrophobic surface. Consequently, if using aqueous phenolic adhesives, the use of surface active wetting agents is strongly encouraged. Furthermore, the hydrophobic surface suggests that non-aqueous adhesives (e.g. polyurethanes) may be effective in bonding spotted gum. While McGavin et al. (2013) found disappointing results with a non-aqueous moisture-cure polyurethane adhesives, it could follow that an alternative polyurethane formulation and/or bonding strategy could demonstrate some promise.
References.


Origin Lab. *Algorithms (Nonlinear Curve Fitting).* Retrieved from


APPENDIX A: Thermogravimetric Analysis

Introduction.

This appendix addresses thermal behavior and percent residue of non-plantation spotted gum and Gympie messmate.

Experimental.

Thermogravimetric analysis (non-plantation spotted gum and Gympie messmate) was conducted using a TA Instruments Q500 TGA. Specimens were milled with a Wiley mill to pass through a 40 gauge mesh. Approximately 20 mg sample was heated in air at 10°C/min (ramp mode) to 600°C. Three replications were conducted per species. Weight and derivative weight versus temperature were determined. Percent residue was determined using the remaining weight at 600°C. Raw TGA data was analyzed using TA Universal Analysis 2000 version 4.5A software.

Results.

Spotted gum and Gympie messmate thermogravimetric profiles and corresponding derivative peaks were determined (Figure 7-1). The first peak (between 25 – 100°C) likely represented specimen moisture loss. Average (standard deviation) weight loss for spotted gum and Gympie messmate was 7.9% (0.2) and 6.5% (0.6), respectively.

The second, third, and fourth peaks roughly corresponded to hemicellulose, cellulose, and lignin degradation, respectively (Cademartori et al., 2013). Differences in species’ thermogravimetric profiles were detected at high temperatures (400 – 600°C) where weight loss was mostly due to lignin degradation (Cademartori et al., 2013).
Figure 6-1: Thermogravimetric profiles (top) and corresponding derivatives (bottom). Non-plantation spotted gum and Gympie messmate.

Non-plantation spotted gum and Gympie messmate showed small amounts of residual ash (after heating to 600°C), suggesting little inorganic matter was present in the two species (Table 7-1).

Table 6-1: Thermogravimetric Analysis Residual Ash Content.

<table>
<thead>
<tr>
<th>Non-plantation Species</th>
<th>Residue Average (%)</th>
<th>STDEV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>spotted gum</td>
<td>0.54</td>
<td>0.22</td>
</tr>
<tr>
<td>Gympie messmate</td>
<td>0.32</td>
<td>0.16</td>
</tr>
</tbody>
</table>
APPENDIX B: Statistical Analysis

Initial contact angles were statistically analyzed using one-way ANOVA. However, data failed to meet two ANOVA assumptions: 1) normal distribution and 2) equal variance (Figure 7-2). This was expected since wood typically displays high data variability due to natural variations. Since sample size was large (> 30) in most cases, violation of normality was not assumed to cause major problems (Pallant, 2007). ANOVA has also been shown to be reasonably robust to equal variance violations (Pallant, 2007). Use of a non-parametric test was examined to address the violation of normality. However, non-parametric tests still require equal variance and thus were not used. Violation of equal variance could be resolved through data transformation, but this technique was not observed in literature’s analysis of contact angle data.

Data variability of initial contact angles was determined and shown in the example box plots (Figure 7-2). Interestingly, heat-treatment caused a decrease in water initial contact angle data variability. While it was possible that heating produced a more uniform, homogenous surface, this decrease in variability could also be caused by some operator error.

Recall that the contact angle on unheated wood decreased rapidly in comparison to that on heated wood. The sessile drop method, static transfer technique was used for conducting contact angle measurements on plantation spotted gum. In performing this method/technique, the specimen surface was manually raised to contact the droplet. Once the droplet detached from the needle tip, the camera began recording images. Any slight operator error would delay image acquisition (i.e. contact angle measurement) and cause higher data variability. Effects of operator error would be more significant on unheated specimens, when the contact angle changed rapidly over time.

Figure 7-2: Initial water contact angle box plots on plantation spotted gum (a: left) and Gympie messmate (b: right) as a function of surface temperature (ºC) during 200ºC heating.
APPENDIX C: Statistic Results

Grit Size Comparison.

One-way ANOVA test with Tukey test means comparison (α=0.05).

<table>
<thead>
<tr>
<th>Species</th>
<th>Liquid</th>
<th>Significantly Different</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>spotted gum</td>
<td>Water</td>
<td>No</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>Formamide</td>
<td>No</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Methylene Iodide</td>
<td>No</td>
<td>0.45</td>
</tr>
<tr>
<td>Gympie messmate</td>
<td>Water</td>
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</tr>
<tr>
<td></td>
<td>Formamide</td>
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<tr>
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<td>Methylene Iodide</td>
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<td>0.20</td>
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</table>

Comparison of Sessile Drop Transfer Techniques.

Two sample t-Test with Welch correction factor (α=0.05).

<table>
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<th>Surface Temp. (ºC)</th>
<th>Water</th>
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<th>p-value</th>
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<tbody>
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<td>0.42</td>
<td></td>
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<tr>
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<td>No</td>
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<td>No</td>
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<td>130</td>
<td>No</td>
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<tr>
<td>165</td>
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<td>0.18</td>
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</tr>
<tr>
<td>192</td>
<td>No</td>
<td>0.15</td>
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</tbody>
</table>

Heating Non-plantation Wood from a Dry State, Initial Contact Angles.

One-way ANOVA test with Tukey test means comparison (α=0.05).

<table>
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<th>Species</th>
<th>Liquid</th>
<th>Significantly Different</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>Formamide</td>
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<tr>
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<td>Methylene Iodide</td>
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</table>
Table 6-5: Methylene Iodide Initial Contact Angles Tukey Test Results.

<table>
<thead>
<tr>
<th>Species</th>
<th>Heat-Treatment Means Comparison</th>
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<th>p-value</th>
</tr>
</thead>
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Heating Plantation Wood from a Water-saturated State, Initial Contact Angles.

One-way ANOVA test with Tukey test means comparison (α=0.05).

Table 6-6: Initial Contact Angles on Spotted Gum Tukey Test Results.

<table>
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<tr>
<th>Heat-treatment Means Comparison</th>
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<th>Formamide</th>
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<tbody>
<tr>
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</tr>
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</tr>
</tbody>
</table>

Table 6-7: Initial Contact Angles on Gympie Messmate Tukey Test Results.