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Energy efficiency of atmospheric pressure plasma-aided porous media surface finishing

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Abstract. Atmospheric pressure plasma pretreatment based on dielectric barrier discharge technology at industrial frequency (50 Hz) has been used for surface activation (oxidation, functionalization) of four species of European and tropical wood samples in a multi-step plasma enhanced capillary process of flame retardancy. Plasma-chemical activation is an effective surface alteration by attaching polar or functional groups to wood and cellulosic surfaces. Oxygen containing functional groups enhance effectively capillary impregnation processes for flame retardation of wood as porous media finishing. Oxidation level was studied by wettability in order to follow the increased surface free energy. For each species, a critical active power surface density was necessary to obtain the best impregnation results more quickly. The relationship between the penetration-spreading parameter and the active power density has been investigated experimentally as process quality parameter.

1. Introduction

In general, the surface free energy (*SFE*) of wood, wooden and cellulosic porous media is not sufficiently high to permit good capillary impregnation by flame retardant containing water solution. In case of finishing such as gluing, painting, varnishing, coating, it prevents better bonding between two or more materials. Hence, for better quality of finishing processes, *SFE* of the low energy wooden surfaces should be increased. The "*open air*", "*non-pressure*" or "*non-vacuum*" atmospheric pressure plasma (*APP-*) pretreatment founded on dielectric barrier discharge (*DBD*) is widely used nowadays for surface activation (oxidation, functionalization) to achieve a higher *SFE* of porous wooden and cellulosic surfaces for enhancement of finishing such as impregnation, gluing, painting, varnishing and coating processes. It is a well-known by the used common three-step impregnation processes to ensure flame retardancy of wood, wooden and cellulosic materials – lumber, timber, paneling, floor, plywood, *MDF*, *OSB*, paper, corrugated board, cardboard [1, 2].

The purpose of this paper is to provide an energy efficiency assessment not only for the *APP*-pretreatment process, but also for the overall plasma enhanced finishing. The ultimate goal of every oxidative *APP*-pretreatment technique is to increase porous media *SFE* or so-called "dyne level", [3, 4, 5], their wettability and capillary activity, as well as to enhance surface finishing by increasing the penetration-spreading parameter (*PSP*) of common process: both *SFE* and liquid *surface tension* (*SFT*) are essential in porous media finishing phenomena. The addition of anionic micelle-forming and trisiloxane-ethoxylate surfactants can reduce the surface tension of a phosphorous flame retardant (*FR*) containing impregnating water solution figure 1.

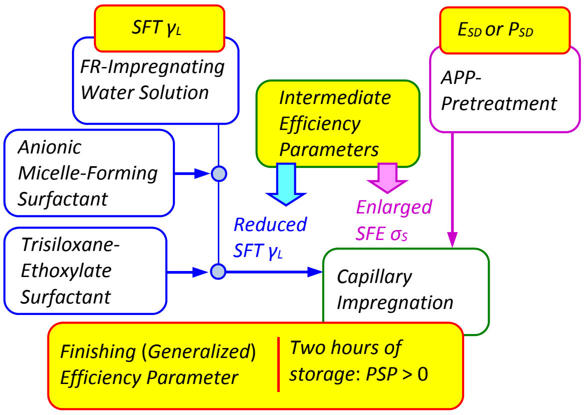

Figure 1. Finishing or generalized efficiency parameter – *penetration-spreading parameter* (*PSP*), and intermediate efficiency parameters expressing an enlarged *SFE* σ_S of the *APP*-pretreated wood surface, and a reduced *SFT* γ_L of impregnating water solution, in a multi-steep plasma-enhanced capillary impregnation process. The relationship between the finishing parameter *PSP* and the active power density P_{SD} (or the corresponding energy dosage E_{SD}) predicts and displays the efficiency of the used plasma enhanced process of capillary impregnation with flame retardant (*FR*) containing water solutions.

Ultimately the energy dosage (or power factor) is known to get a particular wood material to a certain *SFE* or common plasma-aided finishing to a certain *PSP*, it can be used to predict the results if any of the conditional parameters change such as operative speed, duration of treatment or electrode capacity to distribute to necessary level of applied energy (power) equation (1) [3, 5].

2. Factor and parameter of atmospheric pressure plasma pretreatment

The *APP* pretreatment of a wood side in operative gap is done schematically between earthed ferromagnetic (carbon steel) electrode and dielectric barrier (alkali glass) as shown in figure 2. The operating gap between earthed electrode and dielectric barrier was changed from 3 to 15 mm. The high-voltage ferromagnetic electrode was connected to *AC* power supply having high voltage (below 30 kV peak value) and industrial frequency (50 Hz) [6].

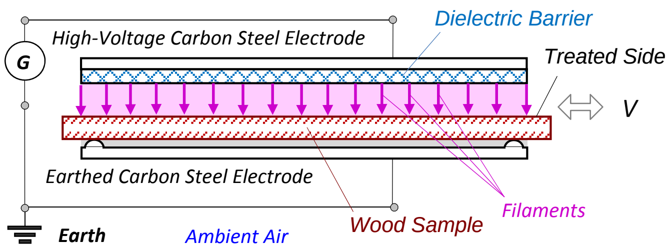

Figure 2. The atmospheric-pressure plasma (*APP*-) pretreatment of a wood surface is done by passing the wood sample through dielectric barrier discharge in air at atmospheric pressure and industrial frequency (50 Hz) created between earthed electrode and dielectric glass barrier in a coplanar electrode system with two structural carbon steel (BDS 2592) electrodes.

2.1. Atmospheric pressure plasma pretreatment terms

As its name suggests "current–voltage" characteristic of a burning *DBD* is a relationship, represented as a chart or graph, between the discharge current flowing through an operating gap and the applied voltage across electrodes. The typical current–voltage characteristic of a burning *DBD* is a relationship between the average current value I_{avg} and the root mean square value of applied voltage V_{rms}: $I_{avg} = \varphi\ (V_{rms})$ [3]. These current and voltage values can be measured directly in an experimental investigation. According to a well-known methodology (*Fillipov-Emelyanov*, 1957) the current-voltage characteristic can be used to establish a new mathematical model of *DBD* behavior – "*active power-voltage*": $P = \varphi\ (V_{rms})$, or "*active power density-voltage*": $P_{SD} = P/S = \varphi\ (V_{rms})$ characteristic, where $S = l\ w$, is the active area of electrode system; l is the length and w is the width of electrodes figures 2 and 4a.

2.1.1. Energy dosage, energy factor or specific energy

The *energy dosage* (E_{SD}) is the specific quantity of *DBD* energy applied to the treated wood surface. This measurement identifies the energy dose E_{SD} as the surface density of discharge energy or specific

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energy (per unit surface) to which a one side or two sides of wood samples is subjected. The being applied active (real, true) power *P*, W; production line speed *V*, m/min; number of side to be treated *N* – one or two; treating surface or electrode width *w* in m, and material dependent D_M, are included in it, figure 2 [3, 4, 5]:

$$E_{SD} = D_M P / (N V w), \text{W min/m}^2. \quad (1)$$

The specific energy E_{SD}, identifies too the *DBD*-energy dosage to which a stationary ($V = 0$) wood surface equals to the electrode surface ($S = l w$) is subjected. The plasma pretreatment time (duration) *t* and the length *l* of treated wood sample (or electrodes) are included in it:

$$E_{SD} = D_M P t / (N l w), (V = 0), \text{W min/m}^2. \quad (2)$$

Sometimes, the energy dosage E_{SD} is called "*watt density*" [3, 4, 5].

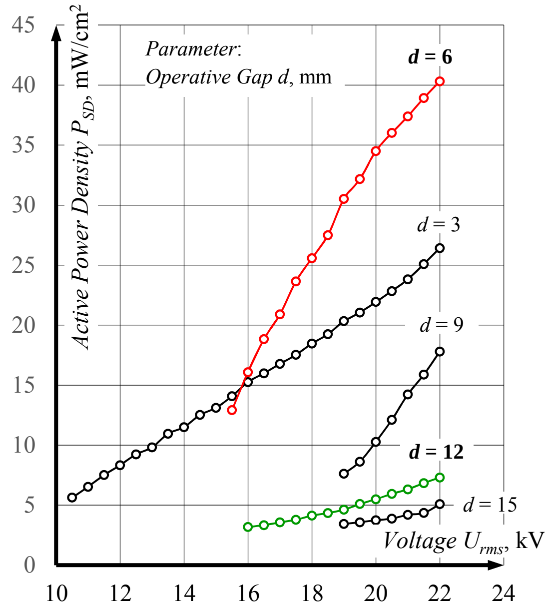

Figure 3. Relationship between *DBD* active power density P_{SD} and applied voltage V_{rms} for different operative gap *d* in the preferred *APP pretreatment* operative area.
Fitting the best trendlines/regression types to experimental data of active power density for two air gap (*d*):

i) polynomial trendline illustrates the relationship between active power surface density (P_{SD}) and voltage (V_{rms}) at air gap $d = 6$ mm:

$$P_{SD} = -0.2292V_{rms}^2 + 12.803V_{rms} - 130.31;$$

ii) polynomial trendline illustrates the relationship between real power surface density (P_D) and voltage (V_{rms}) at air gap $d = 12$ mm:

$$P_{SD} = 0.06\ V_{rms}^2 - 1.5869V_{rms} + 13.191.$$

Notice that the *R*-squared values (R^2) are respectively 0.9990 and 0.9991, which are good fits of the trendlines to the data.

Using this *DBD*-treatment (impact) factor, it is possible to calculate the increase of the *SFE* or to correctly match a *DBD*-treatment device for a particular application.
Once the energy dosage E_{SD} to get a defined wood surface to a certain *SFE* (dyne level) is known, it can be used to predict the results if any of the process parameters change. For example, let's say that the line speed increases from V_1 to V_2 ($V_2 > V_1$):

$$E_{SD} = D_M P_1 / (N.V_1.w) = D_M P_2 / (T.V_2.w);$$

$$P_1 V_2 = P_2 V_1 \rightarrow P_2 = P_1 (V_2 / V_1), \text{ or } P_2 > P_1. \quad (3)$$

If we use a power supply with active power *P*, knowing the energy dosage E_{SD} which is able to get the intended *SFE,* the fastest line speed (*max V*) we can achieve under these conditions well be:

$$max\ V = D_M P / (E_{SD} N w). \quad (4)$$

2.1.2. Power factor or active power density

The active (real, true) power P discloses the ability of a DBD to carry through an effective plasma activation and decides how much faster this activation can be done. The power factor or active power density PSD specifies the power per unit surface of sample subjected to the plasma treatment or per unit length in direction along the production line. The time t defines the length L of the plasma activated surface at a set line speed V ($L = V t$):

$$P_{SD} = E_{SD}/t = D_M P / (N V t w) = D_M P / (N L w), \text{W/m}^2. \quad (5)$$

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It is possible to define a specific power for a certain length L, for example, 1 cm.

The specific active power P_{SD} identifies also the DBD-power density to which a stationary ($V = 0$) treated wood surface is subjected. The plasma pretreatment time (duration) t and the length l of treated wood sample are included in it also:

$$P_{SD} = D_M\, P / (T\, l\, w), \text{ W/cm}^2. \quad (6)$$

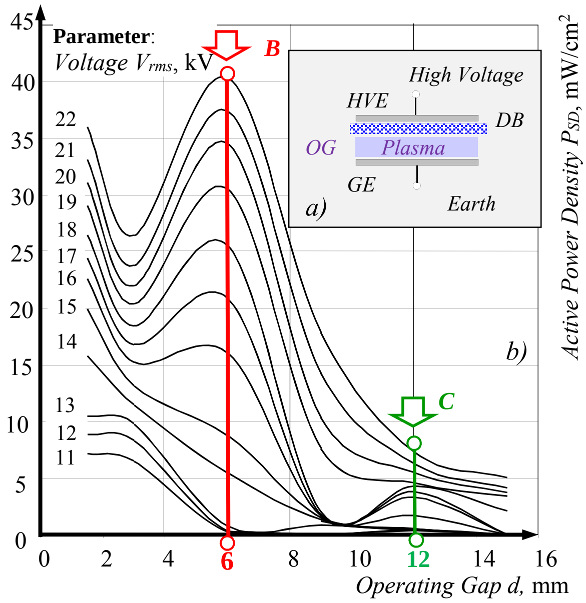

Figure 4. Dielectric barrier air discharge at atmospheric pressure (*DBD*) in asymmetric coplanar electrode system with one glass barrier (***a***), technological *DBD* characteristic "*active power density* (P_{SD}) *–operating gap size* (d)", parameter – applied voltage (V_{rms}), and operational streamer regimes: *regime B* - cathode directed streamers; *regime C* - anode directed streamers, of atmospheric pressure plasma pretreatment at industrial frequency – 50 Hz (***b***).

HVE – high voltage electrode; *GE* – earthed (grounded) electrode; *DB* – dielectric (alkali glass: $\varepsilon_r = 10$; $\rho_V = 10^9\ \Omega$m; $tg\delta = 25$ at 20°C) barrier with $b = 3$ mm; *OG* – operating gap.

The wood samples dimensions (length and width) should be the same as those of the flat electrodes. That is so called power factor of a *DBD* coplanar electrode system.

The effectiveness of a *DBD* can be assessed using that impact factor, or a *DBD*-treatment station can be dimensioned for a specific treatment application. It is very important in order to assess the saturation of plasma activation effect. Also, impact factor can be accepted as an assessment criterion referred to the degree of thermal shock applied to the wood surface by an electrical discharge.

2.1.3. Wood surface treatability

Not all wooden or cellulosic materials can be treated equally well. One of them is very hard to DBD-plasma treatment and requires more treatment energy or power ($D_1 \neq 0$). Another one is less difficult to treatment compared to the previous one ($D_{M,2} < D_{M,1}$). Also, there may be such material that does not require plasma treatment for finishing as their initial surface free energy is sufficiently high ($D_{M,3}=0$). This experimental study was carried out on four kind of wood samples: European white pine (Pinus Sylvestris L) from Bulgaria and three woods from Mexican rain forest: Tzalam (Lysiloma Bahamensis L), Mexican white cedar (Cupressus Lusitanica L), and Mahogany caoba (Swietenia Mahogany L), according a well-known methodology of experiment used by us [1, 2].

The selected wood species form the following range of decreasing density, in kg/m^3: Tzalam - 780; Mahogany caoba - 650; Mexican white cedar – 470; European white pine – 371. There are two hard wood species with high density, D > 540 kg/m^3: Tzalam and Mahogany caoba (Mahogany), and two soft wood species with low density, D < 540 kg/m^3: Mexican white cedar (Cedar) and European white pine (Pine). On the basis of our own former experience in plasma-aided capillary impregnation of wood and wooden materials, an oxidative APP-pretreatment has been applied on the test samples for 60 sec figure 2.

The storage (aging, open) time means a time period after APP-pretreatment which enables an effective plasma-aided finishing processes such as impregnating, gluing, bonding, coating and painting, to be achieved. Plasma pre-activation most often takes place “in-line” immediately prior to the onset of the finishing: the storage time is zero. The storage time should be different from zero when the plasma-aided capillary impregnation is applied in the finishing "out of the line". The substrates with the lowest initial SFE after storage time also have the lowest SFE. This process is commonly described as "hydrophobic recovery" [5]. Comparing the rate of hydrophobic recovery, there is an exception for the mahogany: the mahogany sample with the lowest SFE after treatment has the slowest decrease in surface energy figure 5.

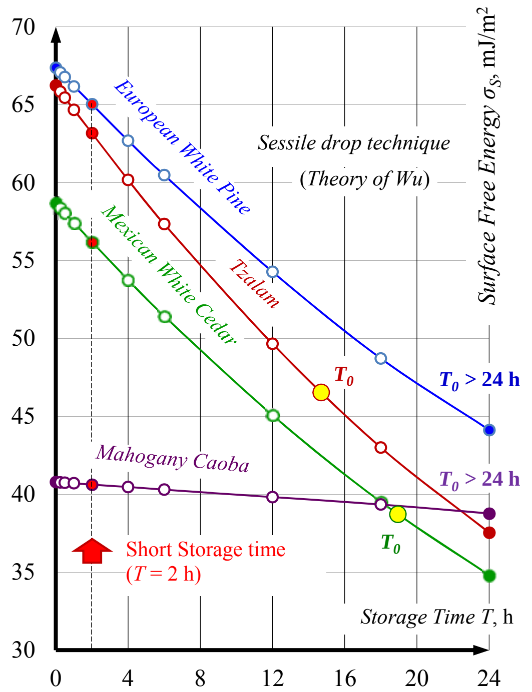

Figure 5. Alteration of the *surface free energy* (*SFE*) σ_S, mJ/m^2, measured by *Sessile drop technique* (*Theory of Wu*) as a function of storage (aging, open) time T, h, after *APP-pretreatment* at 18 kV rms (25.6 kV peak value) and 50 Hz. The measured initial *SFE* were, mJ/m^2: *European White Pine* – 29.86; *Tzalam* – 46.50; *Mexican White Cedar* – 38.59; *and Mahogany Caoba* – 27.87. The short storage time below two hours is suitable for "out of the production line" plasma-aided capillary impregnation process. The *storage time leading to zero effect* (T_0), h, is this storage time that eliminates the positive effect of an *APP-pretreatment.*

Table 1. Storage (aging) time (T) after *APP*-pretreatment and storage time to zero effect (T_0), h.

	Aging time T	0	2	24	T_0
FE, mJ/m^2	Pine	67.37	65.04	44.13	45.19
	Tzalam	66.24	63.18	37.54	15.44
	Cedar	58.70	56.20	34.71	19.04
	Mahogany	40.79	40.62	38.77	190.24

3. Factor and parameter of plasma-aided capillary impregnation

Plasma-aided capillary impregnation finishing will be more successful and the porous media will be more susceptible as the *PSP* >> 0. This is the essence of the rule for obtaining effective plasma-enhanced capillary impregnation finishing. The *PS*-parameter depends only on two thermodynamic factors of the finishing process - the *SFE* σ_S of the wood sample increased by the *APP*-pretreatment; and the *SFT* γ_L of impregnating water solution reduced by the added surfactants. These two factors can be quantified individually at two well-known methods of contact angle measurement - the sessile drop and the pendant drop techniques: $PSP = (\sigma_S - \gamma_L)$.

Studying the relationship between the *PSP* after two hours of storage and the active power density P_{SD} it becomes clear that two effective "*out of the line*" finishing processes are applicable – with *FR-A5* and *FR-A5-S* impregnating solutions: *PSP* >> 0. An effective common process can be realized also with *FR* impregnating solution after an *APP*-pretreatment at P_{SD} > 8.8 mW/cm^2 (15 kV rms; AC): *PSP* >> 0 figure 6.

However, the two modified impregnating solutions *FR-A5* and *FR-A5-S* with low *SFT* provide high *PSP* values (over 15 mJ/m^2) and good impregnation process quality at too low power levels - below 1 mW/cm^2, figure 6.

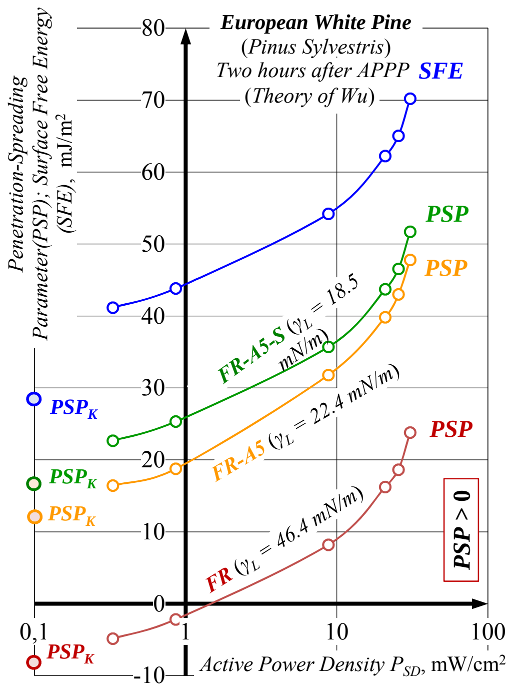

Figure 6. Relationship between the *penetration-spreading parameter* (*PSP*), mJ/m^2, and *surface free energy* (*SFE*), mJ/m^2, measured by *Sessile drop technique* (*Theory of Wu*) and the *active power density* P_{SD} after two hours of storage for *European White* (*Pinus Sylvestris L.*) heart wood samples.

Penetration-spreading parameter (*PSP*) is equal to the minimum *interfacial free energy* (*IFE*) value at $\cos\theta = 1$ ($\theta = 0$ deg): $PSP = \sigma_{SL}$. An *effective finishing* is characterized by a positive value of *PSP*: $PSP > 0$; a non-effective finishing has a *PSP*-value equal or less to zero: $PSP \leq 0$.
Plasma-aided surface impregnation was accomplished by tree types of water solutions of phosphorous flame retardant (*FR*) with different surface tension γ_L: *FR* – bare 30 mass % solution of *FR*; *FR-A5* – *FR*-water solution with micelle-forming anionic surfactant at 5 vol. %; *FR-A5-S* – *FR*-water solution with micelle-forming anionic surfactant at 5 vol. % and trisiloxane surfactant at 0.01 vol. %. PSP_K – *PSPs* of bare or non-treated wood samples.

4. Conclusion

It is often recommended that the active power density applied to the treated side of wood sample during *APP* pre-treatment to be as high as necessary to reach the maximum *SFE* but to be as low as possible in order to save energy – an energy efficiency restriction.

In the present study, contrary to expectations, it has been shown that the "*excessive treatment*" increases *PSP*, although *SFE* is not further increased at higher active power densities, for example over 20 mW/cm^2. The use of reduced *SFT* impregnating solutions allows the use of energy-efficient low active power levels even below 0.33 mW/cm^2.

Acknowledgments

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