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Review Article

Fire Test and Effects of Fire Retardant on the Natural Ability of Timber: A Review

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ABSTRACT

Timber is one of the most sustainable and renewable raw materials available. Globally, it has been increasingly used for the manufacture of home and workplace furniture. Timber products are known to have ignition resistance and a low heat release rate. These characteristics delay burning and maintain the structural durability of a product, protecting both the occupants and their properties in a fire. Timber, however, experiences thermal degradation during combustion, yielding smoke, heat, toxic gases, and char when burned. To understand the fire conduct of timber, extensive knowledge in its process of decomposition is essential. This paper, therefore, reviewed the methods of flammability tests widely employed to investigate the reaction of timber and timber-based product to fire, namely cone calorimeter test, room-corner test, limiting oxygen index (LOI) test, furnace test, and single burning item test (SBI). In addition, an overview of the fire retardant treatments; impregnation and coatings was also presented. The potential effects of fire retardants on the durability, strength, hygroscopicity, corrosion, machinability, glueing characteristics, and paintability of the timber were also highlighted.

Keywords: Fire retardant, flammability test, natural, timber coatings, timber combustion, timber impregnation, wood combustion, wood impregnation

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INTRODUCTION

Despite its numerous benefits, timber application as a constructional material has

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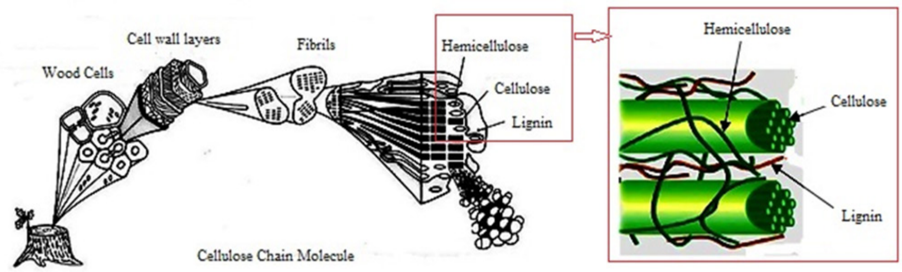
been predominantly restricted by the stigma of burning (Delichatsios et al., 2003; Spinardi et al., 2017). To modify the behaviour of timber and timber-based products towards fire, it is vital to understand the fire conduct and the decomposition process. While it is well-known that timber is not easily burned, it still experiences thermal degradation during combustion, emitting smoke, heat, toxic gases, and char. With regards to the structure or architectural design of timber, it is imperative to perceive the distinction between light timber frame structures, where the fire resistance of wood may be protected by using lining materials such as gypsum and heavy timber structures which frequently depend on the anticipated charring rate (Bisby et al., 2013). Several comparative studies have been conducted on the smoke and heat evacuation from various materials in enclosure fires, extending from the manual counts based on empirical formulae over zone modelling to the utilization of computational fluid dynamics (Merci & Vandevelde, 2007). Nevertheless, limited studies have been conducted on timber and timber-based product.

To improve the ability of timber and timber-based product in fire incidents as to protect the occupants and properties, fire retardants solutions are used. Besides its function as “fire retardant”, much impacts experienced by timber and timber-based product on its natural ability; an area that almost overlooked in the study of the effects of fire retardants. Timber has its own natural ability in surviving the nature such as durability, strength and hygroscopicity. With the addition of fire retarding chemical, the timber and timber based product has also to disclose ability on resisting corrosion, machinability, glueing characteristics, and paintability, but there are not much studies on this especially on various species of tropical timbers. This paper, therefore, aims to provide an overview of the methods commonly employed to investigate the fire properties of timber and timber-based products including the potential fire-retardant treatments; impregnation and coatings. More importantly, this paper also reviewed works that investigated the effects of fire retardants on the natural ability of timber and timber-based products. This review may definitely serve as a starting point for more comprehensive research in the use of timber and timber-based product by providing fundamental information on this particular subject matter.

THE FUNDAMENTAL OF TIMBER BURNING

Generally, each part of a tree is an accumulation of cells which are arranged longitudinally in the stem. These cells are constituted by three main polymers, namely the cellulose (43%), the hemicellulose (28-35%), and the lignin (22-29%). The structural relations between these polymers are portrayed in Figure 1.

When timber is heated to 300°F (150°C), the cellulose, hemicellulose, and lignin are decomposed to unstable gases, tar (levoglucosan), and carbonaceous char (Lowden & Hull, 2013). The decomposition of timber follows a pattern which is considered as the mechanism of superposition of the individual components; starting with the decomposition



(A) **(B)**

*Figure 1***.** (A) Wood cell wall; (B) Macrostructure of fibrils (Hoffmann & Jones, 1989)

of hemicellulose at 180-350°C, followed by the decomposition of cellulose at 275-350°C, and lastly the decomposition of lignin at 250-500°C (Kim et al., 2006). The chemical substance of timber is very similar to sugars as it largely consists of cellulose which is a polymer consolidated by the reoccurrence of glucose. The higher lignin content of timber, however, leads to a higher temperature rate of thermal degradation and its aromatic chemical structure provides a char yield as high as 35-38% at 1652ºF (900°C) (Chung, 2010). At 500°C, the cross-linking response dehydrates the cellulose and the polymerized levoglucosan, producing aromatic structures before transforming to graphitic carbon structures. This process is known as pyrolysis, which is a complicated interconnection subject of chemistry, heat, and mass transfer (Spearpoint & Quintiere, 2001). There are two types of pyrolysis behaviour of solid materials; non-charring and charring. The overall char yield is mainly influenced by the decomposition of lignin (Browne, 1958). The aim of fire-retardants application over timber and timber-based products were to improve both the char production and combustion properties but sometimes only either one of the purpose can be achieved. Investigation on fire properties of Scots pine (*Pinus sylvestris L.*) treated with unmodified and modified silica dispersions, showed no improvement in char yields but the treatment with modified silica dispersions has enhanced the ignition properties including heat release rate (HRR), smoke production, and CO_2 development (Xiao et al., 2016). Conversely, thermal behaviour of oriental beech treated with 0.25%, 1% and 4.70% aqueous solutions of borax (BX), boric acid (BA), BA+BX(1:1), BA+BX(7:3) has decreased the maximum degradation temperature and increased residual char amount (Uner et al., 2016). The char properties of timber reduce the combustion rate and prevent the oxygen from easily entering the combustion zone (Pearce et al., 1981) which is important in fire safety design. The variability of charring rates and other fire properties within species and among different species largely depends on factors including density, moisture content, external heat flux, and oxygen concentration (Friquin, 2010). In timber and timber-based product advanced development, information on charring rate, HRR and the time to flashover are the most valuable information as they probably support either to further investigations, explanations or pass or fail decisions.

During combustion, timber releases smoke which is a mixture of gases, most of which are harmful gases. In fact, it has been reported that about fifty percent of life loss cases in fires are caused by the smoke in the escape pathway and the high rate of toxicity (Drysdale, 2011). The factors influencing the composition of smoke are combustion condition, the pattern of decomposition, ventilation, temperature, and fuel chemical nature (Quintiere, 1982; Rasbash & Drysdale, 1982; Tewarson, 2002). Various compounds are present in the smoke gases from the wood combustion but most methods used to analyse the by-products of fire typically focus on the discharge of carbon monoxide (CO) and carbon dioxide (CO_2) and the decrease in oxygen concentration (Aseeva et al., 2014). Timber assimilates carbon dioxide from the atmosphere as it grows and transforms it into carbon molecules in its cellulose. Combustion of timber reverses this process, whereby about 1900g of carbon dioxide ($CO_{2)}$ is discharged for every 1000g completely burnt timber.

FIRE PERFORMANCE OF TIMBER AND TIMBER-BASED PRODUCT

Fire performance refers to how an object reacts towards the fire. It is subject to the chemical composition and the atomic structure of a material. Identifying the fire performance of a material is vital as it defines the behaviour of fire in relation to a material in the fire incidents. The fire behaviour is a terminology used to depict the intensity, direction, and magnitude of how a fire spreads. The characters of timber in a fire are obtained for various reasons, such as to determine the fire performance of the untreated timber, to evaluate the performance of fire retardant treated (FRT) timber, and for research and development under the umbrella of fire safety engineering. Bench-scale fire test is used to investigate the fire characteristic of FRT and untreated timber by applying a small sample size. Meanwhile, the large-scale fire test is frequently used to test timber as a structural material to provide fire safety classifications for the end-use of it. There are several frequently investigated fire properties and those are important in determining the fire growth, spread, and impact to the occupants as well as the properties (Friedman et al., 2003; Hopkins & Quintiere, 1996; Lowden & Hull, 2013). For instance, (i) the ease of ignition, which defines how prompt the ignition is; (ii) the rate of flame spread, which defines how quick the fire spreads over a surface; (iii) the rate of heat release, which defines how much and how fast the heat is released, and; (iv) the ease of extinction, which defines how fast the flame extinguishes. On the other hand, the characters of smoke from the burning are evaluated in terms of the (i) smoke/toxic gas evolution and the outgrowth rate; and (ii) amount and composition of smoke released during the different phases of a fire.

The hazards of fire make timber an exceptionally attractive element for advanced investigation. The investigation of the fire properties of timber generally will be directed to combustibility test followed by thermal analysis. Timber combustion results in transposition and transformation of the thermochemical and thermophysical aspect of the timber, involving mass loss, heat transfer, pyrolysis, and smouldering. This complex process produces the charring layer which is significant for the fire resistance of the timber and is closely related to the morphology and chemical structure of the timber species. The studies of the morphology and mineral content of the timber species are particularly crucial for the tropical timber species due to their rich and complex anatomy. The influence of these factors on the parameters that define the fire behaviour of timber has been another area of interest for the researchers in this field, whereby observations are often conducted using the scanning electron microscope (SEM).

Combustibility Test

Combustibility is an evaluation of how easily a material blasts into a fire, through flame or burning. Most of the combustibility tests for timber and timber-based products comprise heating a predefined quantity of the test sample for a set span and conducted to collect data on fire properties. The data are used for (i) fire modelling; (ii) prediction of real scale fire behaviour; and (iii) pass/fail tests (Lindholm et al., 2009). There are numbers of test have been developed since the early time in the effort to determine the fire properties of timber and timber-based product. However, the popular methods are cone calorimeter test (Figure 2), room corner test (Figure 3), limiting oxygen index (LOI) test (Figure 4), furnace test and single burning item test (SBI) (Figure 5). Even though the choice of combustibility test is customarily based on the purpose of research but the main concern is the cost involved. To simply understand the aforementioned fire tests, Table 1 detailed the functions and criteria of each test**.**

Thermal Analysis

Thermal analysis is one part of the materials science where the measurements of specified material properties are recorded as they alter from its natural condition due to the change of temperature. Generally, thermal analysis measures three group of physical parameters: (1) mass, (2) temperature or heat flow and (3) other parameters, such as dimension. The thermogravimetric analysis (TGA) is the simplest way of investigating the thermal property of degradation for wood as it provides quantitative information on the decomposition of polymeric substance (Beall & Eickner, 1970; Rowell & Dietenberger, 2012).

Thermogravimetric Analysis. TGA accommodates quantitative data on the decomposition of polymeric material and provides details regarding the degradation kinetics and the char formation (Crompton, 1989). It also analyses the changes in chemical and physical properties of the materials and measures them as a function of increasing temperature

Table 1
Fire Test

Test	Function	Criteria
Cone calorimeter	1. For assortments of the quantifiable combustibility parameters, such as heat release rate (HRR), mass loss rate (MLR), smoke production, and other ignition properties 2. Data obtained from this test is particularly used for the fire retardant study during which it evolves to: (i) Compare the fire reaction of substance to evaluate their fire resistance character for pyrolysis and fire models development; (ii) Procure the substance's specified parameters required as input in the mathematical models for the full-scale room or room/corner test investigation (the data correspond with the results derived from the full-scale room fires tests); and **(iii)** Categorize the substance according to a certain span table for regulatory purposes (Schartel & Hull, 2007) 3. Primary results frequently observed from the cone calorimeter test for timber or timber composites are the curves for mass loss, HRR, and smoke production as a function of time	1. Small-scale test 2. Small sample size (maximum sample size: 100mm * 100mm *50mm) 3. Officially accepted as the International Organization for Standardization (ISO 5660-1) standard to measure the HRR of a specimen in 1993 and the latest version (ISO 5660-2) has been revised in 2002. 4. Test condition is only specific to a well-ventilated fire scenario with constant heat flux 5. Evaluates one-dimensional fire propagation into a sample, considering no surface flame and denying the linking of the results for under-ventilated fires or post-flashover fires (Carpenter & Janssens, 2005) 6. Test according to ISO 5660 could be performed to predict expected test results in EN 13823 – SBI. 7. The cone calorimeter data appear to correspond with the results derived from the full-scale room fires tests (Chung, 2010; Delichatsios et al., 2003; Grexa & Lubke, 2001; Lee et al., 2011; Spearpoint & Quintiere, 2001) 8. Cost beneficial test
Room corner test	1. Measures most of important fire behaviours, including HRR, effective heat of combustion (EHC), MLR, ignitability, production rate of smoke and toxic gases and time to flashover - Flashover is the moment when the total HRR from the entire burning exceeds 1MW, during which the test would be terminated. In a case	1. The test assesses the response of the timber and timber-based wall, surface lining and ceiling products including plywood, chipboards, panels, and wallboards to heat when being installed on the surface of a room and imposed directly to a predefined ignition source at the corner of the room with a single open doorway

Table 1 *(Continue)*

Test	Function	Criteria
	where flashover is not achieved, the test will be prolonged for a maximum of 20 minutes before being terminated 2. Among all the measured fire parameters in a room corner test, HRR and smoke production rate appear to be more dominant (Dillon, 1998), but the time to flashover may be regarded as the most important result of the test (Hansen & Hovde, 2002) 3. Determines the potential of fire growth in a space, whereby the flame spread over the furnishings and the interior finishing materials is considered 4. Considered as a reference scenario test for SBI 5. The test is accepted to be used as compartment fire test apparatus with some modification on its setting of the source of ignition (wooden cribs which are commonly used as the fuel load) and room furniture arrangement (Bartlett et al., 2017)	2. Considered as an ideal real fire model scenario as the material tested is exposed to fire as in orientation that represents the use of the material in actual situation under the well-ventilated conditions 3. The protocols to conduct a room-corner test are restricted to rules and regulations as listed by the internationally recognized bodies; American Society of Testing Materials (ASTM) and the International Standard Organization (ISO); ISO 9705 4. Involve high cost to conduct the test
Limiting oxygen index	1. Defines the minimum percentage of oxygen concentration required to sustain the burning of a material.	1. A mixture of oxygen and nitrogen is passed over a burning specimen positioned vertically in a glass chimney and the oxygen level is reduced until the flame is no longer supported at which the sample burned for a length of 50mmor for a period of 3 min 2. The test protocols can be conducted according to ASTM D286 or the ISO 4589-2 standards
Furnace	1. Determine the charring properties of timber and timber-based products (Bisby et al., 2013; Maraveas et al., 2015; Werkelin et al., 2011; Xu et al., 2015)	1. A furnace is an enclosed structure in which materials are heated up to a considerably high temperature 2. The test protocols are based on the ISO 834-1 (Hugi & Weber, 2012)

Table 1 *(Continue)*

Test	Function	Criteria
Single burning item	1. Timber and timber-based surface lining products are the commonly tested timber product in SBI test (Hagen et al., 2009) 2. The result of the test is used to categorize the building products (non-flooring products) according to its combustibility into Euro classes of A2, B, C, and D 3. The HRR, total heat release (THR), and smoke production rate are measured, while the flame spread and burning droplets/particles are observed visually in this test	1. The sample mounted on a trolley is placed in a frame (made of two vertical wings forming a right-angled corner) under an exhaust system. A triangular shaped propane diffusion gas burner at a HRR of 30 kW is used, representing a burning waste paper basket placed at the basis of the sample corner. The performance of the test sample is observed over a period of 20 minutes before the result is considered for the classification of building materials (Mierlo & Sette, 2005) 2. The test protocols are either the EN 13823 or EN ISO 17025

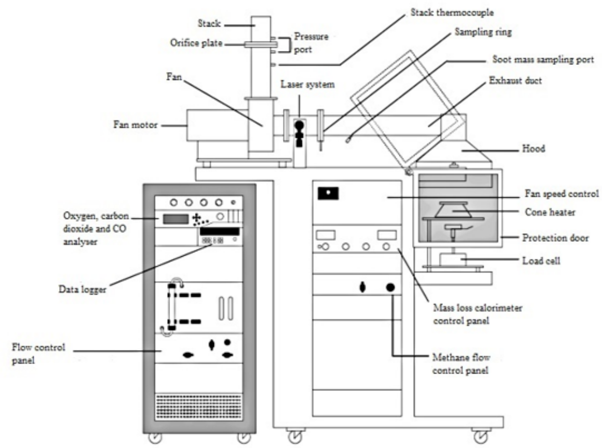


Figure 2. Schematic diagram of a cone (Lindholm et al., 2009)

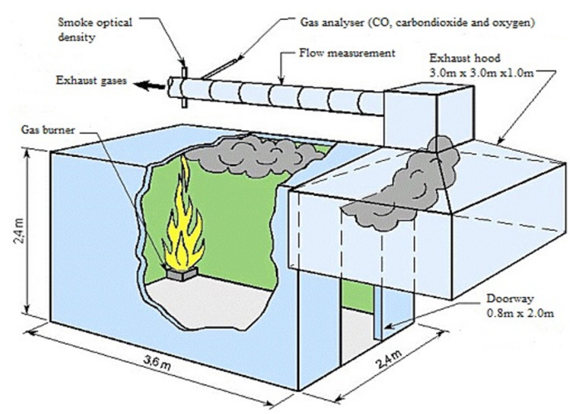


Figure 3. Basic diagram of room corner test (Online image). 2017. Retrieved February 9, 2018 from https://www.sp.se/sv/units/risesafe/safety/fire/PublishingImages/Material/ISO9705-col-txt.gif

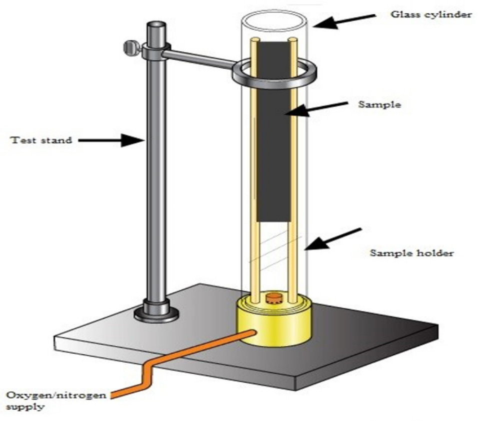


Figure 4. Schematic diagram of LOI test (Online image). 2018. Retrieved February 9, 2018 from http://www.wha-international.com/content/images/3_1_5/o2-index-vert-1.jpg

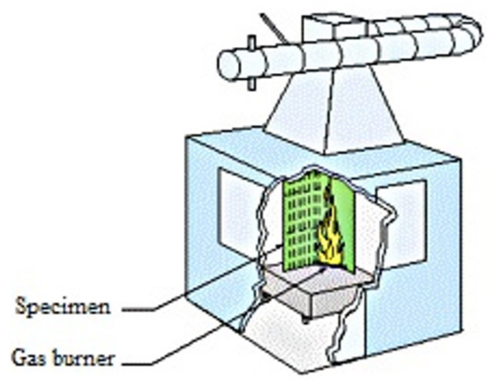


Figure 5. Schematic diagram of SBI test (Online image). 2017. Retrieved February 9, 2018 from https://www.sp.se/sv/units/risesafe/safety/fire/PublishingImages/Material/BildSBI.gif

with the constant heating rate. Thermogravimetric analysis frequently read as a function of temperature under the constant mass loss rate (Coats & Redfern, 1963). Eventually, when the sample (in milligram) is heated, it may lose weight due to its drying or diffusion as gases. In some cases, the substance may increase in weight through reaction towards the test atmosphere (Lowden & Hull, 2013). The mass loss in an inert atmosphere represents the production of fuel after ignition as the concentration of oxygen (O_2) under a flame is nearly 0% (Schartel & Hull, 2007).

Scanning Electron Microscopy (SEM)

It has been claimed by numerous researchers that the charring rate of timber is highly influenced by the anatomy of the timber (Aseeva et al., 2014; Babrauskas, 2005; Giraldo et al., 2016). This charring process is defined as the transformation in the surface structure and ultrastructure of timber during its responses to fire temperatures. The decomposition includes the thermophysical and thermochemical processes on a micro scale. To further investigate the characteristics of timber that influence its reaction to fire, SEM has been substantiated as a suitable instrument for the study of the micromorphology, surface topology, and surface ultrastructure of the biological materials (Echlin, 1968). SEM allows study of the materials in its natural or modified form by generating three-dimensional pictures (Borgin, 1970). Although the resolution of SEM is generally below that of the transmission electron microscope (TEM), this method is widely used to study the anatomical features of wood due to its great depth of field and the relatively easy requirement for sample preparation (Exley et al., 1974). Furthermore, SEM is a microscope that produces a magnified image using the electrons instead of the light. In addition to the timber microstructure, the amount and nature of minerals present can also be observed by SEM (Giraldo et al., 2016).

FIRE RETARDANTS

Fire retardant is a substance used to delay or stop the spread of fire or reduce its intensity. Therefore, to produce a material with satisfactory fire resistance, the products have to be furnished with the most suitable fire retardant substance. A fire retardant material consists of a combination of certain chemicals, which can reduce the flammability of fuels or delay the burning when they are added to the potentially flammable materials, such as textiles, timber, plastics, and others. Fire retardant substances are obtainable mostly in the forms of powder, foam, gel, and liquid to suit the materials that vary in their physical nature and chemical composition. Most fire retardants act as the "synergists" to increase the fire protective benefits. As the elements in fire retardants applied on different materials react differently with fire, the selection of fire retardants must match appropriately to each type of material. In the case of Scots pine treated with phenol-formaldehyde (PF) and melamine- formaldehyde (MF) resins which is known as an efficient strategy to improve timber's dimensional stability, mechanical strength, and durability, have actually caused different fire risk patterns: smoke issues for the PF- treated wood and heat hazard for the MF-treated wood (Xie et al., 2016). In most countries, a clear explanation of the practice of fire safety measures is documented in their national standard of building and fire codes. Generally, building codes incorporate height and area of a room, automatic sprinklers, fire stops, doors and other exits, fire detectors, and type of construction. Meanwhile, the fire codes may contain fire spread, flammability of materials, and fire endurance of a specific material. The common practice may differ with countries.

Timber has been utilized for most applications due to its poor thermal conductivity properties. Fire retardants have been developed to reduce the flammability of timber and encourage the char forming. The use of fire retardants for timber has started back when the Romans treated their ships with alum and vinegar for protection against fire, followed by Gay-Lussac using the ammonium phosphates and borax to treat the cellulosic textiles (Rowell & Dietenberger, 2012). In 1895, The U.S. Navy again enforced the utilization of fire retardants for their ship. This development was further applied in the building construction in 1899 when the City of New York required the use of fire retardants for a 12-storey building (Rowell & Dietenberger, 2012). In relation to the timber and timber-based products, the commonly applied methods to improve its fire retardant trait are impregnation and coatings (Davidson & Freas, 1987; Horrocks & Price, 2001). The selection of fire retarding methods largely depends on the suitability and cost involved. The impregnation of fire retardants including polyphosphatic carbamate, and ceramic coatings including alkoxy metal salt improved the fire performance of Japanese red pine (*Pinus densifl ora Siebold et Zuccarini*) and Japanese linden (*Tilia japonica Simonkai*) (Harada et al., 2007). Table 2 illustrates the six categories of fire retardant treatment for timber (LeVan & Winandy, 2007).

Table 2

Fire retardant treatment

Chemical	**Effect to timber**
Ammonium dihydrogen orthophosphate	Promote the formation of increase char at a lower temperature
Bromine, chlorine	Free radical trap in flame
Sodium silicates (non-intumesce), polyol+phosphoricacid +dicyandiamide/melamine/ urea/guanidine (intumesce)	Coating the timber surface
Metal alloy	Increase thermal conductivity of timber
Dicyandiamide and urea, borax	Dilute the combustible gases from the timber with non-combustible gases
Ammonium phosphate	Reduce the heat content of volatile gases

During the development process of an improved fire retardant, the tested FRT timber-based products undergo a credential bench-scale fire test which would then indicates the success or failure of the retardant improvement. The result from the bench-scale test can be used as input data to model the prediction of fire effects in different scale incident (Xu et al., 2017). The selected FRTs can be further tested in a large-scale fire test, which is costlier to accomplish the required rating. The ways to measure the performance of a fire retardant are presented in Table 3 (Rowell & Dietenberger, 2012).

Table 3

Fire retardant test

Test	**Expected Result**
Thermogravimetric analysis (TGA)	The weight of the sample recorded as a function of time at a constant temperature
Differential thermal analysis (DTA)	Amount of heat by measuring temperature differences between the sample and an inert reference
Differential scanning calorimeter (DSC)	Actual differential heat flow is measured when the sample and reference temperature are equal.
Cone calorimeter	Ignition time, mass loss rate (MLR), combustion products, heat release rate (HRR), and other parameters as a function of time
Tunnel flame-spread tests	Surface flame spread
Critical oxygen index test	The minimum concentration of oxygen in an oxygen-nitrogen mixture

Timber impregnation

The timber impregnation is conducted to stabilize the dimension, increase the strength and resistance to water, and reduce cracking of the timber. This process involves pressure-impregnation of chemical solutions using full-cell pressure processes (provided this is the most effective way to instil chemicals into the timber). The penetration of the chemicals highly depends on the species, microstructure, and moisture content of the timber. Three softwoods, Sugi (*Cryptomeria japonica*), Korean pine (*Pinus koraiensis*) and Hinoki (*Chamaecyparis obtusa*), vacuum–pressure impregnated with a fire retardant chemical consisting of ammonium phosphate polymer (APP), guanyl urea phosphate (GUP), phosphonic acid and minor amount of additives reduced the modulus of rupture (MOR) and static modulus of elasticity (MOE) compared with before treatment; conversely, the dynamic modulus of elasticity (DMOE) increased after treatment (Wen et al., 2014). There have been studies done to improve the ability of absorption or permeability of timber by the fire retardants, such as by having an additional step of microwave heating. This microwave pre-treatment is claimed to be able to increase the permeability of wood significantly for the substance such as metal alloy (Torgovnikov & Vinden, 2010; Vinden et al., 2011). For instance, the poplar samples impregnated with the ammonium polyphosphate (APP) fire retardant after being pre-treated with microwave heating demonstrated a significant improvement in its fire resistance (15.89% less at peak HRR, 5.69% less at total HRR, and 13.59% less at total smoke production, TSP) as compared to those without pre-treatment with microwave (He et al., 2015). The nano technology development has contributed not a small impact on the fire retardants research and development. The nano-silver solution as fire retarding formulation has significantly increased the fire retarding ability of four hardwood and one softwood species that is commercially used in the various industrial application in Iran (Taghiyari, 2012). Furthermore, the wood nanotechnology has allowed the Balsa wood (*Ochroma pyramidale*) to be delignified to form a hierarchically structured and nanoporous scaffold mainly composed of cellulose nanofibrils. These nanocomposites are impregnated with colloidal montmorillonite clay to form a nanostructured wood hybrid of high flame retardancy (Fu et al., 2017). This impregnation is almost similar to the chemical preservative treatments of timber except that there are higher retentions and absorption of chemicals acquired for the fire-retardant protection. The compounds which are highly reactive to the hydroxyl groups of cellulose, hemicellulose, and lignin components include epoxides, isocyanates, anhydrides, lactones, and diols (Mathias et al., 1991). It has been reported that the nitrogen-phosphorus impregnated Poplar and heat treated at 150°C decreased the moisture sorption by 57%, while the leach resistance values (LRV) increased by 70%, thus enhancing the fire retardant performance of the wood (Chu et al., 2017). Thermally treated Spruce demonstrated lower weight loss in fire resistance test (Čekovská et al., 2017). A significant change in the thermal properties of treated sawdust reveals that the impregnation of hydrated-sodium metaborates into sawdust could create a significant amount of condensed phase char and provide a highly effective fire retardant protection with multiple modes of action (Nine et al., 2017). Apparently, combination of heat treatment and impregnation technique with improved formulation has further enhanced the timber's reaction to fire and its working properties. Additionally, the Poplar wood treated with nitrogen and phosphorus (NP) based fire retardants and impregnated with polysodium silicate-aluminum dihydrogen phosphate (PSADP) also reduce the hygroscopicity of the wood, increase its LRV by 81% and reduce the moisture absorption rate by 40.3%, as compared to the wood which has been treated with NP but without PSADP (Zhang et al., 2016).

Timber Coatings

Another way to provide varying degrees of fire retardant to timber against fire is coatings. A coating is defined as an intelligible layer formed from a single or multiple application of a coating material to a substrate (DIN EN ISO 4618; 2.52). The fire performance of edge-jointed lumber of A*lbizia* and *Gmelina* improved with the application of trimethylol melamine phosphoric acid coating (Subyakto et al., 2003). As indicated in the current standard (DIN EN ISO 4618; 2.53) a coating material is a material in fluid, paste or powder form which, when applied, forms a defensive and ornamental coating. Coating materials are complex chemical products including lacquers, paints, and other similar products. In most cases, coatings comprise of binders (also known as the film formers), pigments and extenders, solvents, and additives. Application of fire retardant coatings is to provide fire retardant properties, such as low flame spread, low smoke emission, and non-toxicity, without altering the performance of the substrate (U.S. Patent 6245842, 2001). In addition to its main function as a fire retardant, an ideal timber coating is also defined based on its effect on the hydrophobicity, toughness, oxidation protection, UV resistance durability (Liu et al., 2017). It has been proven that a hydrophobic coating based on synthetic resins and waxes exhibits a better durable performance against weathering and a higher hydrophobicity after 6 weeks of weathering, as compared to coating based on zirconium nanoparticles in butanol (Pánek et al., 2017). Coatings products are easy to apply using spray, brush or rollers. Generally, there are two types of coatings: (1) intumescent and (2) non-intumescent. Intumescent coatings will 'intumesce' to form an expanded low-density film on the surface of a material to protect the lower layer against the high temperatures and oxygen when exposed to fire. Prior reviews on the research and development of intumescent coatings have been reported by Vandersall (1971) and updated later by Kay et al. (1979). The intumescent coatings formulated through the combination of a dehydrating agent (e.g. polyammonium phosphate) a char former (e.g. starch, glucose, and dipentaerythritol) and a blowing agent (e.g. urea, melamine and chlorinate paraffin). Coatings that use additives, such as boric acid, borax, chlorinated compounds, and antimony trioxide required an additional binding substance. As for the wood plastic composites (WPC) which could be widely used in the residential construction and the decking and furniture industry, the addition of 5 wt% of zinc borate (ZB) or manganese dioxide (MnO_2), montmorillonite (MMT), and stannic oxide (SnO_2) into intumescent flame retardants (IFR) created a fire retardant WPC with a V0 rating, exhibiting an excellent fire retardancy (Ren et al., 2015). As for the advancement in binder-free coatings, hexagonal boron nitride (h-BN) nanosheets with anisotropic thermal conductivity and low thermal diffusivity and effusivity properties made a high-performance binder-free fire-resistant coating for wood up to 900 °C (Liu et al., 2017).

Formulation of Retardants

Chemicals used in the composition of fire retardants of timber range from the inexpensive inorganic salts to the more complex and expensive chemicals. Fire retardants are generally categorized by their corresponding chemical formation: (1) brominated, (2) phosphorus, (3) nitrogen, (4) chlorinated, and (5) inorganic (Davidson & Freas, 1987). Inorganic salt is the most used type of fire retardant for timber (LeVan & Winandy, 2007). It is frequently used for interior timber products due to their good performance on mechanical and thermal properties, optical behaviour, and higher bacterial resistance (Kartal et al., 2007). Examples of the inorganic salts are monoammonium sulfate, diammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, silicon dioxide, titanium dioxide, sodium silicates, and boric acid. The inorganic salt, such as silicates and borates may involve a slow impregnation up to 24 hours (US4612050A, 1986) and according to the fact that timber is a highly hydrophilic material, this situation is undesirable in some cases. The solubility of the inorganic salts in water highly depends on zinc chloride as it is the most soluble salt (2 g/ml) while boric acid is the least soluble salt (0.056 g/ml) (Merck Index 1968). Consequently, it appears that borax could possibly be used in the WPC as fire retardants since the presence of boron after leaching has been shown with SEM-EDX and LOI tests (Cavdar et al., 2015). Timber treated with sodium borate (agricultural borax) which is environmentally friendly solution, performed better resistance to burning (Sogutlu et al., 2011). In the process of looking for "green solvent", a new formulation for impregnation of Norway spruce (*Picea abies*) has proposed the application of the ionic fluid 1-ethyl-3-methylimidazolium chloride as a carrier for calcium metasilicate, titanium dioxide, and tungsten trioxide (Croitoru et al., 2015). The prevalence of ionic liquids as a method for impregnation is the application of environmentally friendly solvents, but there is a need for more findings on application to other species of timber.

Effects of Fire Retardants on the Main Characteristic of Wood

The goal of applying fire retardants to material whether by coating, impregnation, soaking or other possible ways, is to provide fire retardant ability to the material. The selection of formulation is always based on the natural level of fire retardant ability of the material which differs from one material to another. The fire retardants may increase the natural characteristic of the material or decrease it. In the case of a timber, which is one of the natural materials utilized in the interior and exterior products, the application of fire retardants has been shown to improvise and optimize its fire retarding performance (Ayrilmis et al., 2007; Bajaj, 1992; Camino et al., 1989; Goldstein & Oberley, 1966; Hao & Chow, 2003; Liu, 2000; Nine et al., 2017; Ostman & Tsantaridis, 1995). However, in the attempts to reduce the flammability rate of timber, the fire-retardants treatment may change its natural characteristics, including the durability, hygroscopicity, strength, corrosivity, machinability, surface appearance, gluability, and paintability (Ayrilmis et al., 2007; Bekhta et al., 2016; Chu et al., 2017; Hirata et al., 1991; Jiang et al., 2015; LeVan & Winandy, 2007; Wang, 2010). FRT timber regularly becomes moisture sensitive, discoloured or corrosive (Laranjeira et al., 2015). In order to investigate the pressure effects on the thermal degradation of FRT timber; the Sugar pine, Douglas-fir and California black oak treated with ammonium sulfate, boric acid, borax, diammonium phosphate zinc chloride were tested with differential scanning calorimetry (DSC) at 0, 10 and 30% moisture content and under 4 different pressure accordingly (Woo & Schniewind, 1987). The magnitude of the side effects, such as an increased moisture content, pressure effect, a reduced strength, and an increased potential to corrode metal connectors, relies on the fire-retardant chemicals utilized. The acceptance of the side effects depends on the intended use of the products.

Durability. The durability of timber refers to the ability to resist elemental and natural forces of decay. There have been studies in the USA and the UK which investigated the adverse effects of fire retardants on wood (Östman et al., 2001). The general practice used to evaluate the durability level of FRT timber is the comparison of fire performance prior and after weathering. This weathering phase may by natural exposure or accelerated. Application of FRT timber in the exterior requires durability in humid conditions when exposed to rain, good LRV, and resistance to weather including the UV radiation. In many circumstances, FRT timber appears to be moisture sensitive, discoloured, corrosive, and mechanically weak, making it not durable in the exterior applications. The degradation may result from the fungus that could be caused by the cycles of rain, moisture, termites, putrefaction, and destructive insects. Most of the fire retardant formulations increase the durability in some characteristics but decline others. Decay resistance tests revealed that solid wood specimens treated with quaternary ammonia compounds didecyl dimethyl ammonium chloride (DDAC) and didecyl dimethyl ammonium tetrafluoroborate (DBF) showed resistance against the fungi tested, however, monoammonium phosphate (MAP), diammonium phosphate (DAP) and ammonium sulphate (AS) did not provide complete protection but inversely the DDAC and DBF resulted higher HRR compared to MAP, DAP and AS (Terzi et al., 2011). It has been reported that the graphite (G), aluminium trihydrate (ATH), and titanium oxide (TiO_2) prevent the discolouration of the wood-polypropylene composites under the accelerated weathering of a xenon-arc lamp source during 1000h but reduce the tensile properties (Turku & Kärki, 2016). Furthermore, the stabilized WPC with aluminium hydroxide as fire retardant has shown a lower fading degree but a reduced outdoor durability (García et al., 2009). The expandable graphite (EG) and ammonium polyphosphate (APP) has been demonstrated to improve the flame retardancy of acrylonitrile–butadiene–styrene-based WPCs but worsen the mechanical properties (Zheng et al., 2014). Overall, the timber treated with inorganic salt is suitable for application where the humidity never exceeds eighty percent, which corresponds to the water-soluble properties of the fire retardant and hygroscopic properties of the timber. As for exterior application, higher leach resistance is desirable to increase the durability of the timber.

Strength. Fire-retardant treatment may incur a reduction in the strength properties of the timber (Croitoru et al., 2015; Davidson & Freas, 1987; Kadir et al., 2015; LeVan & Winandy, 2007; Mathias et al., 1991). In some cases, physically observed conditions have demonstrated that in the length of three to eight years of service, timber would turn brash, brittle, and fragmented. The main factors that decrease the strength of FRT timber are the thermal degradation, chemicals reaction, and effect of elevated temperature (LeVan & Winandy, 2007). FRT timber roof and truss members which are imposed for thermal degradation have shown a loss in bending (and possibly tensile) strength (Kasal, 1999). Most of the fire-retardant substances did not increase the strength properties of timber. Furthermore, the addition of ammonium polyphosphate (APP) and silica as fire retardants could cause a reduction in the mechanical properties of the composites wood-fibre/polypropylene (PP), except for the tensile strength of the small amount of silica-filled wood-fibre/PP composite (Zhang et al., 2012). The use of wood flour enhances the mechanical properties of thermoplastics but additionally increases the burning rate of WPC (Arao et al., 2014). The combination of elevated temperature conditions and the acidic nature of the fire retardants may have accumulated the rate of acid hydrolysis of the timber and reasoned the loss of strength and embrittlement of FRT timber (LeVan & Winandy, 2007). This finding explains the long-term impact of elevated temperatures and acids on the composition of the FRT timber. To effectively measure the strength properties of FRT timber, mechanical test could be conducted or strength losses for any combination of exposure conditions and times may be calculated by assuming that the total strength loss due to fire retardant treatment and thermal exposure is the sum of an intrinsic loss due to physical changes, and a loss due to chemical changes which is measured by the fractional conversion (Berndt & Schniewind, 1990). The requirement for the strength of FRT timber has been stated in some building codes including the International Building Code (IBC), the ANSI/TPI 1-2014 National Design Standard for Metal Plate Connected Timber Truss Construction, and the ANSI/AWC NDS-2015 National Design Specification (NDS) for Timber Construction. Due to the strength issue, most of the building codes require some reductions in the design values and the capacity of connectors used in conjunction with the treated timber.

Hygroscopicity. Hygroscopic is an ability of a substance exposed in the room temperature to absorb and adsorb water from the surrounding atmosphere. It may modify the original features and properties of the exposed substance, such as an increase in volume, boiling point or viscosity as the water molecules become trapped in between the molecules. Physically, a hygroscopic substance tends to become damp and waterlogged when exposed to the surroundings containing salt and sugar. Based on the existing studies, timber treated with inorganic fire-retardant salts are more hygroscopic than the untreated timber (Ayrilmis et al., 2007; Winandy et al., 2002), particularly at a high relative humidity. One of the initial problems associated with hygroscopicity of the FRT timber is the corrosion of metal fasteners and fittings such as metal truss plates. An alternative solution to decrease the hygroscopic effect using the silicon compounds and nano-wollastonite-based substance may be considered (Cai et al., 2016; Fufa et al., 2010; Soltani et al., 2016). The combination of sodium silicate, boric acid, ammonium borate, and di-ammonium phosphate has been shown to improve the leaching resistance, while the formulation of sodium silicate boric acid and di-ammonium phosphate increases the hygroscopic property and the metal corrosive efficacy of Japanese pine (*Pinus densiflora*) (Won et al., 2014). There have been limited studies on the hygroscopicity effect of FRT timber, instead, more research works have been done to investigate the hygroscopicity level after heat treatment, elevated temperature, against humidity, and other properties (Kumar & Shakher, 2016; Martin et al., 2013; Time, 2002).

Corrosions. Metal fasteners have a vital function in the development of timber construction. Nevertheless, these fasteners are subject to corrosion that could decrease the capacity of the structural joint. The inorganic salt fire-retardant compounds for timber are corrosive to metals in the humid or moist environments. Furthermore, the hygroscopicity characteristic of the FRT timber may impose aggressive corrosion even at a low relative humidity. The degree of corrosions by FRT timber varies according to the formulation of the chemical involved. Based on a 3-year corrosion test of eleven wood fastener materials in the wood treated with copper-containing waterborne salt additives, the fastener materials that are cathodic with respect to copper should be selected when a long service life is needed under wet conditions (Baker, 1980). The application of FRT timber in the exterior has been a case of study in many countries with some reports made accessible. In relation to the historic buildings in the Czech Republic, the original roof timber was seriously corroded by the ammonium phosphate and sulfate-based fire-retardant coatings, whereby repetition of coating led to an accumulation of salts in the timber and caused an undesirable side effect of structural elements thinning (Kucerova et al., 2007). Some formulations including the corrosion inhibitors, such as sodium dichromate and ammonium thiocyanate have been reported (Tuomi, 1980). Nonetheless, the reports on the resistance to corrosion with the non-leachable type of fire retardant for timber remain limited. One aspect that has gained little attention in the exterior usage of timber is the fungal attack. Therefore, the formulation of borate-based fire retardants such as zinc borate does not only benefit the timber in biostatic, tannin stain resistance, flame retardant properties, corrosion prevention but also renders the use of a separate dry film fungicide unnecessary (Schoeman & Lloyd, 1999). As the usage of FRT timber expands globally, the building codes have evolved accordingly. Since 2009 to 2015, there has been a serial revision for the International Building Code (IBC) under the section 2304.9.5; "Fasteners in preservative-treated and fire-retardant-treated wood". The revisions include many new subsections (2304.9.5.1 through 2304.9.5.4) dealing with timber treatments in a different condition of environmental applications. Specifically, the subsection 2304.9.5.3 as shown in Figure 9, states that fasteners (including nuts and washers) utilized with FRT timber in exterior or in other wet or damp condition, must be hot-dipped zinc-coated galvanized steel, stainless steel, silicon bronze or copper. This segment permits other types of fasteners (barring nails, wood screws, timber rivets, and lag screws) to be mechanically galvanized as per ASTM B 695, Class 55 at the minimum.

2304.9.5.3 Fasteners for fire-retardant-treated wood used in exterior applications or wet or damp locations. Fasteners, including nuts and washers, for *fire-retardant-treated wood* used in exterior applications or wet or damp locations shall be of hot-dipped zinc-coated galvanized steel, stainless steel, silicon bronze or copper. Fasteners other than nails, timber rivets, wood screws and lag screws shall be permitted to be of mechanically deposited zinc-coated steel with coating weights in accordance with ASTM B 695, Class 55 minimum.

Figure 6. Section 2304.9.5.3 of the 2012 IBC (Online image). 2015. Retrieved February 9, 2018 from http://seblog.strongtie.com/wp-content/uploads/2015/04/figure1.jpg

Machinability. Machinability of wood means the ability of wood to undergo typical machining process such as sawing, milling or drilling. There is no clear clarification on the indicators that can directly relate to the machinability of timber. The performance of timber and timber-based product in machinability frequently measured by relative indicators which used to have high connection on the physical process and the results generally referred under identification of cutting resistance of the timber. Torque and axial force have been selected as relative indictors for machinability of innovative wood based materials with addition of styrene-butadiene rubber (SBR) gum granulate in the effort of determination of its cutting resistance by Wilkowski et al., 2014. The machinability of drilling process of hardboard and novel wood-fiber material with lignins as binder has been investigated with three relative indicators of machinability taken into account: cutting power, the specific cutting coefficients associated to torque and the specific cutting coefficients associated to the thrust force for variable cutting parameters (three cutting speeds, five feeds rate) (Wilkowski et al., 2011).

There are only a few studies of the machinability of FRT timber available and mainly on the practice of the machining process (Davidson & Freas, 1987). The regular practice of preparing FRT timber for trimming and mouldings is to cut the timber approximately to the finished size prior to the treatment to minimize the machining (Davidson & Freas, 1987). This is because of the appearance of salt crystal in FRT timber which has harsh effects on the cutting tools. The use of regular high-speed steel tools may only allow cutting of not more than a few hundred feet of the FRT timber. An increased tool life is obtainable by using the cutting and shaping tools tilted with tungsten carbide or similar abrasion-resistant alloys (Davidson & Freas, 1987; Kultermann & Spence, 2016).

Gluability. Gluability of timber is often recognized as evaluation of shear strength of timber at the glued joint. Since the early years, the intended end-use of the timber and timber-based product determines the formulation of the glue. Classified as the thermosetting polymers, phenol resorcinol-formaldehyde (PRF) provides excellent weather, water, and humidity resistance when cured for interior or exterior uses but has a poor effect on the FRT timber. The deterioration rate of wood glue joints of the epoxy resin is the highest, followed by the aquapolymer-isocyanate resin, and lastly the resorcinol resin (Wang et al., 1993). Timber of the Southern pine species treated with ammonium salt fire retardant, glued with resorcinol-resin adhesives under conventional gluing conditions (hot-press phenolic adhesives) resulted in a lower joint quality as compared to the similar untreated specimens in block-shear evaluation (Schaeffer, 1966). To enhance the gluing characteristic of FRT timber, a combination of resorcinol-resin glue with a liquid formalin hardener have been proven to produce better joints and structural bonding than the glues with paraformaldehyde hardener when cured at 65°C or higher temperature (Schaeffer, 1966).

In recent years, with the increasing awareness towards safer environment, apparently there are advancement in the fire retardants formulation. Plywood prepared from Poplar veneers glued using urea formaldehyde resin and treated with seven different fire retardant compositions passed the glue shear strength test according to Indian Standard (IS) (Samani & Khali, 2016). Additionally, the sol-gel technique enables timber to be permanently silified to a specific degree by coating or impregnating it with chemically or physically modified silica sols, which has considerably improved the fire retardancy and perform better gluing properties (Mahltig et al., 2008).

Paintability. Generally, the fire-retardant treatment of timber has no conflict with the decorative paint coatings, except for the treated timber which has accumulated moisture content. With regards to the timber treated with hygroscopic inorganic salts, the moisture content must be reduced to twelve percent or less when applying the coating. In the exposure to a relatively high humidity, an element of crystallization can be seen over the surface of the paint coatings applied on the timber treated with hygroscopic salt. The natural finishes used for the fire-retardant treatments may vanish as the treatment and subsequent drying may cause darkening and irregular staining on the painted surface. To overcome this situation, manufacturers usually prepare a decorative fire-retardant timber by gluing a thin and untreated decorative veneer facing the treated core. The effects of fire retardants on the paint applied on FRT timber have not been extensively studied, with only limited research reporting the effects of paint on the combustion resistance of untreated timber and the development of paint formulation as fire retardants (El-Wahab et al., 2010; Staggs et al., 2003).

CONCLUSION

Timber is one of the most sustainable, appealing, versatile, durable, eco-friendly, and renewable raw material available. The past years have witnessed growing interests in the use of timber and timber-based products in building construction and furnishings with present practices seeing its vast potentials to be further developed for various uses. However, in some circumstances, the utilization of timber and timber-based products is unfeasible due to its combustible properties, which may cause unwanted fires that could cause fatalities to the occupants and damage to properties. Therefore, the usage of timber is limited by certain safety requirements and regulations. In order to enhance its reaction to fire, timber and timber-based products are treated with fire retardants and surely safety requirements to fulfill such as performance requirements lined by the American Wood Preservers' Association and may differs according to region and country. Fire retardants generally decrease the effective heat of combustion, the initial peak heat release, and the average heat release rate. On the contrary, the ignition times are usually increased and have minimal impact on charring rates and the fire endurance of structural members. The excessive levels of fire retardants can increase the production of smoke. FRT timber and timber-based product also results in reduction in their mechanical properties and become more brittle compared to the untreated.

From this review, it can be concluded the issues of thermal degradation and fire performance of solid timber, FRT timber and timber products in either elevated temperature or direct fire exposure circumstances are most likely overlooked. Although considerable studies have been done on some species of timber and timber-based product, the finding is not feasible for generalisation even for the same category of timber due to complexity of the processes involved. This situation leaves many gaps in attaining full understanding of thermal degradation and fire behaviour of solid timber, FRT timber and timber-based products especially for the tropical species. Additionally, there are not many in-depth studies focusing on the effects of fire retardants on the ability of strength, durability, hygroscopicity, corrosion, machinability, glueing and paintability of different species of commercially traded timber and timber-based products across the world.

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