STUDY ON FIRE PROCESS KINETICS OF PARTICLEBOARD

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SUMMARY

Fire-retardant particleboard has been studied in Vietnam recently. There are many factors affecting the quality of fire-retardant particleboard, in which the factors of fire process kinetics are very important. Fire process kinetics is expressed through multiple criteria, such as thermal conductivity, mass loss rate of the samples, temperature change in the samples, time to spread fire, time to flame, smoldering time of particleboard, etc. The purpose of this research is to study the kinetics of fire process of particleboard produced from *Styrax tonkinensis* wood and 3 fire-retardant mixture formulas, then select a fire retardant mixture formula suitable to technology and production conditions in Vietnam. The study results showed: 1) The 3 fire retardant formulas enable to produce fire-retardant particleboard which meet the basic requirements of particleboard used in construction and furniture. The requirements include: good fire resistance, less effect on board strength, etc. Among these 3 fire-retardant mixture formulas, the third one is most suitable to the current production conditions in Vietnam; 2) During the studying on kinetic factors of fire process, we can propose the solutions to prevent and fight fires and thereby giving the technology suitable with specific technology and production conditions; 3) Production technology of fire-retardant particleboard, according to the research results, can be applied entirely on practice production with the equipment used in the common particleboard production nowadays.

Keywords: Fire-retardant mixture, fire-retardant particleboard, mass loss rate, smoldering time, thermal conductivity, time to flame, time to spread fire.

I. INTRODUCTION

In recent years, particleboard material is gradually replaced natural wood and widely used in construction and furniture. However, particleboard is highly flammable. Therefore, the study to produce fire-retardant particle board plays an important role in fire prevention, and the competitive ability of particleboard on the market. In the world, fire prevention for wood and wood materials is one of the mandatory criteria of product quality. Currently, the countries producing more fire-resistant particleboard are Russia, China, the US, Sweden, Canada, Japan, Germany, etc. There are many methods of fire-retardant particleboard production, however, in summary, two main methods are: fire-retardant treatment for the last particleboard product and fire-retardant treatment during manufacturing process. The most common method today is: The fire-retardant is mixed with glue, and then the mixture is sprayed into wood chips.

In Vietnam, the particleboard production technology is in the first period with few plants and factories producing common particleboard. The fire-retardant particleboard type has not yet any production facility. Due to poor moisture resistance and fire prevention, the common particleboard has gradually lost its position in the market. The scientists from Vietnam National University of Forestry and Vietnam Academy of Forest Science have studied and produced fire-retardant particleboard since 1996.

There are many directions to study fire prevention, such as study on fire retardant, fire prevention methods, testing methods of fire resistance... However the kinetic study of combustion process of particleboard is the most complete study and very important. It suggests suitable fire retardants and fire prevention methods and thereby contributes to the fire prevention, fire disaster reduction, and product quality improvement, cost lowering.

In this paper, we present a research methodology of kinetic study of combustion process of particleboard produced from Styrax tonkinensis wood and 3 fire-retardant mixture formulas.

II. MATERIALS AND METHODS

2.1. Raw materials used in the experiments

2.1.1. Raw wood and wood chips

Wood used in the experiments is *Styrax tonkinensis* – Pierre (group VII) at the age of 7-8 years old, harvested from Doan Hung District, Phu Tho Province.

Styrax tonkinensis wood is flammable, sapwood and heartwood are differentiated, light color, straight and smooth grain, no taste, earlywood and latewood are differentiated, cellulose content 47-49%, lignin content 22.3%, wood density 0.41g/cm^3, shrinkage coefficient 0.29, longitudinal compression strength 19.2 MPa, static bending strength 50.5 MPa, low natural durability, easy workability and easy to crack.

With these characteristics, based on the requirements of the materials used in particleboard production, it can be concluded: *Styrax tonkinensis* wood meet the requirements for production of wood particleboard.

After harvesting, *Styrax tonkinensis* wood was debarked and produced wood particles on BX444 wood chipper machine at Center of Forest Industry, Vietnam National University of Forestry. After sorting, removing unsatisfactory wood chips, chips were dried to a moisture content of 3 - 5% for core layer, 4 - 6% for surface layer and screened their size. The test results showed that:

Surface layer particles: Mainly particles are 0.25mm in thickness, but there are some slightly thicker (>0.25 mm). Meanwhile, thickness of the standard particle is 0.15-0.25mm. Mostly surface layer particles are less than 10 mm in length, while standard particle's length is 20 mm. The slenderness of the surface layer particles is about 40-50 (requirement of the standard is 100 - 200).

Core layer particles: The particles are mainly more than 0.35 - 0.45 mm in thickness, some of them are 1-2 mm, while thickness of the standard particle is 0.35 - 0.45 mm. Mostly particles are less than 30mm in length (about 23 mm). The best length for core layer particles is 40 mm. The slenderness of the core layer particles is about 40 - 50 (requirement of the standard is 60).

With such characteristics, showed that the particles producing at the Center of Forest Industry, Vietnam National University of Forestry only met the length requirement. The other indicators were not satisfied and need for subsequent treatment.

2.1.2. Adhesive

Adhesive used in the experiments was Urea-formaldehyde glue (U-F) with commercial name Dynchem WG -2888 supplied by DYNO company.

The technical specifications of the adhesive U-F according the testing standards GB/T14074.4-93: liquid; milky; solid content: 47%, density: 1.25-1.27 g/ml; viscosity: 100-180 Pa.s (at 20^{0}C); pH: 7.0-7.2; gel time: 67 s; free formaldehyde content: less than 0.5%, storage time: 2 months.

With such technical specifications, U-F adhesive can fully meet the requirements of an adhesive used for particleboard. The amount of used glue was 10% for the surface layer and 12% for the core layer particles.

2.1.3. Water resistance substance

Based on published results of research and production, a paraffin emulsion produced in Guangdong - China was used to enhance water resistance for the fire-retardant particleboard in this study.

The paraffin emulsion was colorless, insoluble in water, glue, and alcohol; soluble in ether, CCl_4, etc. Technical specifications: density: 0.835-0.855g/cm^3; solid content: 60-65%; melting temperature: 60°C; decomposition temperature: 170°C; burning temperature: 360°C.

In this research, the paraffin emulsion was used at the weight of 1% in comparison with particle mass.

2.1.4. Fire retardants

The chemicals were produced in Duc Giang Chemical Factory.

Boric acid (H_3BO_3): Boric acid is a white crystalline substance, molecular weight: 61; density: 1.44g/cm^3; soluble amount in water: 20°C-5g/100g H_2O; melting temperature: 70°C; decomposition temperature of 320°C; pH: 4.

$Na_2B_4O_7.10H_2O$: $Na_2B_4O_7.10H_2O$ is a white crystalline substance, molecular weight: 382; density: 1.55 g/cm^3; soluble amount in water at 20^{0}C: 3.75g/100g H_2O; melting temperature: 87°C; decomposition temperature: 387°C; pH: 9.3.

Fire retardant UP {H_3PO_4 1 mol; Urea 1.5mol}: UP is a fire retardant generated when H_3PO_4 reacts with urea; yellow transparent, solid content: 55-65%; pH: 6.5-7, density: 1.21-1.25g.ml^{-1}; ability to completely soluble in water at 20°C: 321g/100g H_2O; viscosity: 80-100 Pa.s (at 20°C); storage time: 6 months.

$Na_2HPO_4.12H_2O$: $Na_2HPO_4.12H_2O$ is a white crystalline substance; solubility in water at 20°C: 6.3g/100g H_2O, at 100^{0}C almost soluble.

$(NH_4)_2HPO_4$: $(NH_4)_2HPO_4$ is a white crystalline substance; solubility in water at 20°C: 6.3g/100g H_2O, at 70°C: 106g/100g H_2O.

2.2. Experimental methods

2.2.1. Fire-retardant particleboard production

Process of making fire-retardant particleboard is presented in Figure 1.

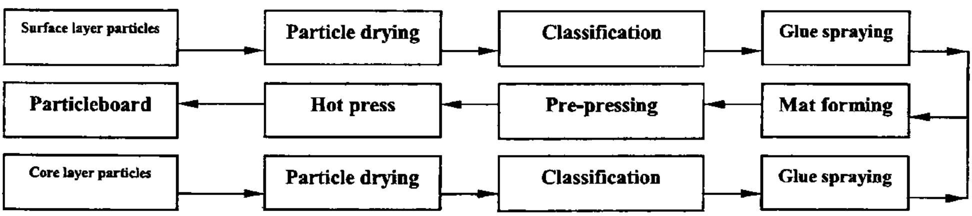

Figure 01. Technical process of making fire-retardant particleboard

The technical process of making fire-retardant is essentially similar as the process of creating common particleboard. The main difference is the method of providing fire retardants into particleboard. In this study, the fire retardants were mixed with the glue during glue application stage.

The 3 fire retardant mixture formulas used in the study were as follows:

Formula 1: $Na_2B_4O_710H_2O$ 50%; H_3BO_3 50%.

Formula 2: $Na_2HPO_412H_2O$ 55%;

$(NH_4)_2HPO_4$ 10%.

Formula 3: H_3PO_4 1mol ; Urea 1.5mol.

Fire retardants in formulas 1 and 2 were separately dissolved in water at temperature of 50°C to supply solutions at a concentration of 50%. After the fire retardant dissolved totally in water, these solutions were mixed with the glue. The fire retardants in formula 3 can be directly mixed with the glue. The amount of fire retardants added to the glue was 10%

(compared to the amount of glue). The mixing process of the fire retardants and the glue, the spraying process of the glue mixture into particles all needed to be stirred carefully to avoid lump creating. Viscosity of the glue mixture can be reduced by raising its temperature to 30 - 40°C.

The technical parameters of particleboard before pressing: moisture content of the particles before mixing with the glue mixture: surface layer: 4 6%, core layer: 3 5%; moisture content of the particle mat after mixing with the glue: 15%; the pH after mixing with the glue: surface layer: 6.5, core layer: 5.5.

The technical parameters of fire-retardant particleboard: thickness: 16 mm; density: 0.7g/ cm^3; the structure rate 1: 3: 1; moisture content of the particleboard after hot pressing 10%; the mechanical and physical properties met the requirements of particleboard at level II used for furniture and construction. The hot pressing parameters: temperature: 160°C, pressure: 2.2 MPa, pressing time: 0.4 min/mm.

2.2.2. Testing methods

Quality of the glue were tested according to the standard GB/T4897-77.

pH values of the glue, fire retardants, paraffin emulsion and mixture of these substances were measured by pH meter (HI 9224 Microprocesser printing pH meter). The accuracy of pH meter was 0.1. Viscosity of the glue is measured by viscometer (RionViscotester VT-04). Bonding strength (shearing strength perpendicular to the board surface) assessing effects of fire retardants on bonding quality of the particleboard was tested according to the standard GB/T 14074.10-93. The testing equipment is a mechanical testing machine AMSLE 5 tons 11/2612 of VNUF. Gel time of glue was tested according to the standard GB/T 14074.10-93.

After hot pressing, the fire-retardant particleboard is stabilized for 48 hours, then dried to a moisture content of 12% (moisture meter Wagner L606). The accuracy of the moisture meter was 0.1%. The specimens were cut following kinetic testing standards.

Fire resistance of particleboard (mass loss rate) was tested according to ASTM-E69-50. Testing equipment was a "fire tube".

Specimen's mass change speed depending on temperature and temperature in the specimen were tested according to the standards ASTM D192 and ISO871. Testing equipment was the "fire tube" and a "ceramic box".

Specimen's mass change depending on temperature was measured with an electronic scale (Ohaus Precision standard). The accuracy of the electronic scale was 0.01 g. The highest mass of the specimen can be measured as 2000 g.

Temperature change in the specimen was measured by a thermometer (Sense Tech Meter 150). Technical characteristics of the thermometer were as follows: measuring range: 0 - 1700°C, resolution: 1°C, accuracy: 0.1°C.

Time to spread fire, time to flame, and moldering time of the particleboard were tested according to JIS Z2120. Testing equipment was the "fire tube"

III. RESULTS OF THE EXPERIMENTS

3.1. Technical specifications of the glue mixture

To ensure the quality of particle board, technical specifications of the glue mixture, fire retardants, and water resistance substance were checked. The pH, gel time, solubility, bonding strength are presented in Table 01.

Table 01. Technical specifications of the glue mixture

Formula	Technical specifications		
	pH	Gel time (s)	Bonding strength (MPa)
Control (0)	7.1	67	1.81
1	5.1	41	1.50
2	5.6	50	1.69
3	5.8	55	1.78

Testing results of solubility of fire retardants revealed that the fire retardants in formula 3 can dissolve unlimitedly in water. Therefore the chemicals in formula 3 could mixed directly with the glue U-F. The fire retardants in formula 2 were difficult to dissolve in water so the temperature of the mixture needed to be increased to 40°C. In formula 1, each chemical $Na_2B_4O_7.10H_2O$ or H_3BO_3 was poorly soluble in water, but when mixed them together, the solubility was better. Therefore, in the particle drying process, the amount of water used to dissolve the fire retardants needed to be calculated.

The results in Table 01 showed that pH of the glue mixtures were not suitable to spray into particles (pH requirements for surface layer particles: 6.5; core layer particles: 5.5) [3]. The fire retardants in formula 1 most affected pH of the glue mixture, followed by formula 2 and 3. Hence, pH values of the glue mixtures would affect bonding quality of the fire-retardant particleboard. Due to the fast curing time, the glue film was brittle, bonding quality was reduced. This was also proved by the bonding strength results, only in case of formula 3, the bonding strength almost reached the requirement. With the other formulas (1 and 2), the bonding strength values were lower than the requirement.

Therefore, when producing fire-retardant particleboard by mixing the fire retardants and glue, it is necessary to check and adjust pH value of the glue mixture.

3.2. The change velocity of mass loss rate

The change velocity of mass loss rate according to the specimen's temperature is presented in Table 02.

Table 02. The change velocity of mass loss rate (%)

Fomula	Mass loss rate (%)					
	100°C	200°C	300°C	400°C	500°C	600°C
Control (0)	6.56	8.63	14.20	28.81	39.80	42.11
1	5.90	6.70	7.90	14.92	22.61	24.30
2	6.00	6.20	7.70	13.11	21.61	23.42
3	6.40	6.90	8.11	17.21	24.82	26.71

From the data in Table 02, the following correlation equations were received:

$$Y_0 = 21.667 + 0.237T - 10^{-3}T^2 - 9.2.10^{-3}T^3$$

$$Y_1 = 15.167 + 0.135T - 5.1.10^{-4}T^2 - 4.4.10^{-7}T^3$$

$$Y_2 = 15.028 + 0.129T - 4.710^{-4}T^2 - 3.9.10^{-7}T^3$$

$$Y_3 = 18.064 + 0.17T - 6.4.10^{-4}T^2 - 5.6.10^{-7}T^3$$

The results in Table 02 showed that: The mass loss rate of common particleboard changes very quickly when the temperature changes (velocity of temperature increase on the specimen surface was Vmax = 50°C). When the temperature increased, the mass loss rate of fire-retardant particleboard also increased. However, at low temperature periods (<300°C), the mass loss rate changed almost insignificantly. Only when the temperature increased 400-600°C, the mass loss rate of the fire-retardant particleboard types increased significantly. The mass loss rate of the fire-retardant particleboard with increasing temperature can be placed in the following order: control particleboard > fire-retardant particleboard from formula 3> fire-retardant particleboard from formula 1> fire-retardant particleboard from formula 2. So the formula 2 revealed highest fire resistance. However, it should be noted that the fire-retardants in formula 2 caused difficulty in particleboard making processes due to poor solubility of the chemicals in water.

3.3. The temperature change in the specimen

The temperature change in the specimen over time to flame are presented in Table 03.

Table 03. The temperature change in the specimens

Formula \ Temperature (°C)	Time (minute)			
	10	20	30	40
Control (0)	127	230	384	658
1	100	185	330	600
2	96	161	310	591
3	113	206	367	621

From the data in Table 03, the following correlation equations could be received:

$$Y_0 = 126.75 - 3.91\tau + 0.43\tau^2$$

$$Y_1 = 123.75 - 6.67\tau + 0.46\tau^2$$

$$Y_2 = 150 - 10.66\tau + 0.54\tau^2$$

$$Y_3 = 106.75 - 3.27\tau + 0.40\tau^2$$

From the results in Table 03 and the correlation equations, it is shown that: When the specimens were burned in a fire tube, if the burning time increased, the internal temperature of the specimens increased. When the burning time <30 minutes, the temperature raise slowly. From 10-30 minutes the temperature inside the specimens increased, but very slowly, however, as the burning time > 30 minutes, the temperature inside the specimens increased rapidly.

The temperature inside the fire-retardant particleboard from formula 2 increased very slowly, follows were formulas 1 and 3. This disclosed the ability of thermal conductivity and thermal radiation of particleboard from formula 2 is highest.

3.4. Time to spread fire, time to flame, and time of smoulder

Time to spread fire, time to flame, and time of smoulder of particleboard are presented in Table 04.

Table 04. Time to spread fire, time to flame, and time of moulder

Formula	Time to spread fire (s)	Time to flame (s)	Time of smoulder (s)
Control (0)	24	120	80
1	58	25	48
2	60	23	36
3	43	42	24

Note: The data in Table 04 is the average values of the tests.

The results in Table 04 showed that the common particleboard have shorter time to spread fire, longer time to flame, and longer time of smoulder compared to the fire-retardant particleboard types in the same conditions of paraffin rate and other technological parameters.

The time to spread fire of the particleboard could be arranged in order: the fire-retardant particleboard from formula 2 > the fire-retardant particleboard from formula 1 > the fire-retardant particleboard from formula 3. The time to flame, and time of smoulder of the fire-retardant particleboard could be placed in the following order: the fire-retardant particleboard from formula 3 > the fire-retardant particleboard from formula 1 > the fire-retardant particleboard from formula 2; and the fire-retardant particleboard from formula 1 > the fire-retardant particleboard from formula 2 > the fire-retardant particleboard from formula 3 in the same conditions of paraffin rate and other technological parameters.

These results can be explained as follows:

When temperature in the fire-retardant particleboard increases, inside water starts to evaporate. When the temperature less than 150°C, the fire-retardant particleboard becomes lighter due to evaporation of water, in fact this is the stage of surface water removing, free water release. Number of chemicals such as CO, C_2H_5OH, H-CHO escape from the fire-retardant particleboard. The fire retardants belonging Bo group are analyzed at temperatures higher than 70°C and create HBO_2, $H_2B_4O_7$. H_2O, $Na_2B_4O_7\,10H_2O$, these chemicals are dehydrated at temperature more than 40°C. Paraffin melts at 70°C. So at this stage, some chemicals is effective against fire, the chemical reactions have not happened. As the temperature continues rising, the substances in the particle board starts to analyze. At a temperature of 220°C, wood is pyrolyzed and generates flammable substances with low molecular weight.

At a temperature of 220   280°C, cellulose is dehydrated and generates coal, steam, CO, CO_2, etc. The fire retardants are strongly analyzed. $(NH_4)_2HPO_4$ is analyzed and generates NH_3, $NH_4H_2PO_4$, H_2O, HPO_3. The fire retardants from Urea and H_3PO_4 are analyze at 190°C and generate NH_3, P, CO, P_2O_5. $Na_2HPO_412H_2O$, at 200°C release 12 H_2O molecules. Thus, at this stage all the fire retardants are analyzed and generate substances effective against fire.

At the temperature from 300-500°C, the mass loss rate of the particleboard increases. Mass loss rate of the control particleboard has exceeded the permitted limit (20%). Meanwhile, that of fire-retardant particleboard is still in the permitted limit. During this period, there are many products of pyrolysis process, the oxidation reaction occurs very strong, the flame burning process starts happening. The flame burning process have led to the burning process of solids. The volatiles generate much during this period. The flame burning process depends on the low molecular weight substances evaporated during heat analyzing.

In the period from 280   365°C, the chemical reactions occur strongly. Speed of cellulose analyzing is fastest. Cellulose is polymerized and creates left glucose, resin, and continue generating CH_4, H_2, and oil. This period causes less effect on lignin. The analyzing substances from fire retardants are effective on fire prevention. They dilute combustion gases, reduce heat conduction inside the fire-retardant particleboard.

When the temperature reaches 500 - 600°C, mass loss rate of fire-retardant particleboard and control particleboard are all exceed permissible limit. This is the stage of smoulder and create a lot of smoke. In this phase, the velocity of mass loss rate increases very slowly. This can be explained as follows: the gaseous and liquid products are very less (1.7%). The particleboard has transformed into a different material (coal). The fire retardants containing phosphorus creates P_2O_5 and immediately reacts with charcoal under the reaction: $P_2O_5 + 5C \rightarrow 2P + 5CO$. The reactions in the direction of creating CO and reducing CO_2/CO causes effect of lowering the heat of exothermic reactions, because the oxidation of C creates CO and 110.4KJ/mol, and the oxidation of C creates CO_2 and 394.7KJ/mol. Fomulas 2 and 3 are happenned with this mechanism.

In the fomulas 2, both of $(NH_4)_2HPO_4$ and $Na_2HPO_4.12H_2O$ contain phosphorus component. When the temperature rises, $Na_2HPO_4.12H_2O$ dehydrates, melts and creates a coating layer effective against fire with flames and fire spread. $Na_2HPO_4.12H_2O$ dehydration process causes the process of heat absorption. $(NH_4)_2HPO_4$ is effective against spread of fire, smoke and fire burning with flames. $(NH_4)_2HPO_4$ increases the water realease 3 times compared with common particleboards, and lowers CO escape. Due to having phosphorus component, fomular 2 and fomular 3 induce least time of smoulder after leaving ignition sources.

The ingredient of fomular 1 including $Na_2B_4O_710H_2O$ and H_3BO_3, under heat effect, they are analysed, and creates B_2O_3 and steam effective in prevention of flame and fire spread. However, the ability to control the smoke of the substances in Bo group is lesser than that in the formulas 2 and 3. Therefore, the time of smolder in particleboard of fomula 1 is longest (48-53s). Meanwhile, time to spread fire, time to flame, and time of smoulder of the control particleboard is longest. This shows that common wood particle boards made of *Styrax tonkinenesis* wood is flammable material.

IV. CONCLUSION

From the above results, we can give some conclusions:

We can fully control the fire provention process of particleboard by the kinetic parameters of the combustion process. The success kinetic study can completely replace the conventional research methods while controlling the combustion process.

The fire-retardant particleboard produced from the 3 above fire retardant mixture formulas showed good quality and met the requirement of particleboard in level II using for furniture and construction. Among these 3 fire-retardant mixture formulas, the third one is most suitable to the current production conditions in Vietnam. The chemicals in formular 3 have very good solubility in water, cause less effect on bonding quality and less difficulty on particleboard production technology, and result in effective fire resistance.

Production technology of fire-retardant particleboard, according to the research results, can be applied entirely on practice production with the equipment used in the common particleboard production nowadays.

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NGHIÊN CỨU ĐỘNG HỌC QUÁ TRÌNH CHÁY VÁN DĂM

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TÓM TẮT

Nghiên cứu, tạo ra các loại ván dăm chậm cháy đã được các nhà khoa học nghiên cứu tại Việt Nam khoảng 5 năm trở lại đây. Một số loại ván dăm chậm cháy đã được sản xuất thử nghiệm. Có rất nhiều các yếu tố ảnh hưởng tới chất lượng ván dăm chậm cháy, trong đó các yếu tố về động học quá trình cháy của ván là hết sức quan trọng. Động học quá trình cháy được thể hiện qua nhiều chỉ tiêu, như: hệ số dẫn nhiệt, tỷ lệ tổn thất khối lượng mẫu thử, sự thay đổi nhiệt độ bên trong mẫu, thời gian bén lửa, thời gian cháy có ngọn lửa, thời gian cháy âm ỉ của ván dăm... Mục đích của bài viết này là nghiên cứu động học quá trình cháy của ván dăm từ gỗ Bồ đề và 03 đơn pha chế chất chống cháy, qua đó tìm ra đơn pha chế chất chống cháy phù hợp với điều kiện công nghệ và sản xuất của Việt Nam. Kết quả nghiên cứu cho thấy: (1) 03 đơn pha chế chất chống cháy cho phép tạo ra được ván dăm chậm cháy, đáp ứng được yêu cầu cơ bản của ván dăm dung trong đồ mộc và xây dựng. Các yêu cầu đó gồm: khả năng chống cháy tốt, ảnh hưởng ít đến độ bền ván... Trong 3 đơn pha chế chất chống cháy, đơn thứ ba là phù hợp nhất với điều kiện sản xuất của chúng ta. (2) Khi nghiên cứu được các yếu tố động học của quá trình cháy, chúng ta có thể đề ra các giải pháp phòng, chống cháy và qua đó đưa ra được các công nghệ phù hợp với từng điều kiện công nghệ, sản xuất. (3) Công nghệ sản xuất ván dăm chậm cháy, theo kết quả nghiên cứu hoàn toàn có thể áp dụng vào thực tế sản xuất với những trang thiết bị dung trong sản xuất các loại ván dăm thông dụng hiện nay.

Từ khóa: Chất chống cháy, động học quá trình cháy, hệ số dẫn nhiệt, sự thay đổi nhiệt độ bên trong mẫu, thời gian bén lửa, thời gian cháy âm ỉ, thời gian cháy có ngọn lửa, tỷ lệ tổn thất khối lượng, ván dăm chậm cháy.

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