Distilled Spirits Lees Ash as Cement Additive

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The voluminous generation of distilled spirits lees (DSL) in China presents a challenge for proper disposal and potential environmental pollution. In an effort to address this issue, this study aimed to find a resourceful solution for DSL utilization. The application of incinerated rice husk ash as a mortar supplementary material in cement provides an innovative solution for the disposal of DSL. Five samples of distilled spirits lees ash (DSLA) were produced using both muffle furnace (MF) and fluidized bed (FB) combustion at different temperatures. The properties of DSLA were characterized through measurements of specific surface area and observations using scanning electron microscopy (SEM). Mortar specimens were prepared by replacing 10% of cement with DSLA, and strength tests were conducted. The SEM results revealed the crisscross mesh structures in the DSLA samples. Additionally, the findings indicated a strong connection between the specific surface areas and the micromorphology. In this work, all DSLA samples, except for the one produced in FB at 800 °C, could improve compressive and flexural strengths in the prepared mortar specimens and were suitable for employment as cement additives.

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INTRODUCTION

As a major liquor-producing nation, China boasts over 37,000 liquor factories, and the total amount of distilled spirits lees (DSL) produced in China reaches up to 15 million tons per year (Xu *et al.* 2009). DSL, generated during the unique solid-state fermentation process for producing distilled spirits, are perishable because of their high moisture content (around 60 wt%) and strong acidity. To improve the effectiveness and the yield of the liquor, rice husk is usually added to sorghum during the fermentation process, resulting in DSL containing a high content of rice husk (40 to 50%) (Xu *et al.* 2007).

Although traditionally the DSL were used as animal feed because of their high nutritional content, advances in biotechnology have resulted in their digestible nutrition becoming too low to meet the requirements of livestock feed (Liu *et al.* 2001). As a result, DSL are now primarily disposed of as waste, causing serious environmental pollution (Deng and Luo 2004). Nevertheless, recent research has shown that the DSL can have potential for use as a runoff and soil loss control agent (Hazbavi and Sadeghi 2016), as well as a raw material in the production of activated carbons and other hypersorbents (Chen and

Zhao 2013). These studies demonstrate the potential of DSL as a valuable resource, beyond its traditional uses.

As a type of special biomass resource, DSL can also be combusted to generate power or heat. However, combustion of DSL in grate chain stock boilers is difficult and inefficient, leading to challenges and incomplete combustion (Xu *et al.* 2007). The use of circulating fluidized bed decoupling combustion technology has been explored as a method to achieve efficient combustion of DSL with low NOx emissions (Yao *et al.* 2011; Zhu *et al.* 2015; Han *et al.* 2016). After incineration, DSL contributes about 5% of its weight to distilled spirits lees ash (DSLA). The proper disposal of DSLA is an important research focus. Considering the high concentration of silica in rice husk, which is a common component of DSL, proper combustion conditions can result in the production of a high pozzolanic material known as rice husk ash. It has been shown to have pozzolanic effects and can be used as a cement additive in previous studies (Jauberthie *et al.* 2003; Saraswathy and Song 2007; Chindaprasirt and Rukzon 2008; Nair *et al.* 2008; Zerbino *et al.* 2011; Awad *et al.* 2018).

In this study, different DSLA samples were obtained at different conditions. Then, the properties of DSLA were investigated through the use of X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and nitrogen adsorption specific surface area tester. The study aimed to determine the feasibility of using DSLA as a cement additive in concrete by blending it into the mixture and evaluating the resulting compressive and flexural strengths at different ages (3 days, 7 days, and 28 days). This study provides a new solution for the disposal of distilled spirits lees and adds to the existing body of experimental data for the potential industrialization of DSLA as a cement additive.

EXPERIMENTAL

Materials

Distilled spirits lees ash

The DSL used in this study was sourced from Luzhoulaojiao Corporation Ltd. in Luzhou China. The results of the proximate and ultimate analyses are listed in Table 1.

Table 1. Proximate and Ultimate Analyses of Raw DSL

Proximate Analysis (%)				Ultimate Analysis (%)				
Moisture	Volatile	Ash	Fixed carbon	C_{daf}	H_{daf}	N_{daf}	O_{daf}	S_{daf}
59.80	28.30	5.10	6.80	50.20	7.20	3.90	38.40	0.30

daf: dry ash free

The preparation of DSLA samples was conducted using alternately a muffle furnace (MF) and a fluidized bed (FB) made in the Circulating Fluidized Bed Laboratory of Harbin Institute of Technology. The MF used in this work was manufactured by Changsha Youxin Industrial Co., Ltd. (Changsha, China), and it has a temperature range from ambient temperature to 1000 °C with a heating ramp for 5 to 10 °C/min. The raw DSL was introduced into approximately 1/3 of the volume of a 90 × 60 mm^2 crucible, and the thermal treatment was completed in the MF with its door half opened to allow for complete combustion with sufficient oxygen. The heating temperature (600 and 700 °C) and time (1

h) were controlled, with a heating ramp of 5 °C/min. The schematic of the FB used in this work is shown in Fig. 1. It consisted of five sections: the reaction section, feed section, temperature control section, gas supply section, and ash collection section. The FB reactor, which has a height of 600 mm and an inner cylindrical diameter of 30 mm, was heated by three resistance wires surrounded by refractory and insulation materials. There are three K-type thermocouples that can measure the temperature at different positions, and the average temperature was used as the bed temperature. The raw DSL was added to the FB using a screw feeder. In the FB, the DSL was incinerated at three bed temperatures (600, 700, and 800 °C). The DSLA was generated and separated by a cyclone separator and collected for further experiments and tests.

Different samples were designated with unique names throughout this paper. For example, MF-600 denotes the DSLA sample produced at a temperature of 600 °C in MF, while FB-600 denotes the DSLA sample produced at a temperature of 600 °C in the FB. MF-700, FB-700, and FB-800 have similar meanings.

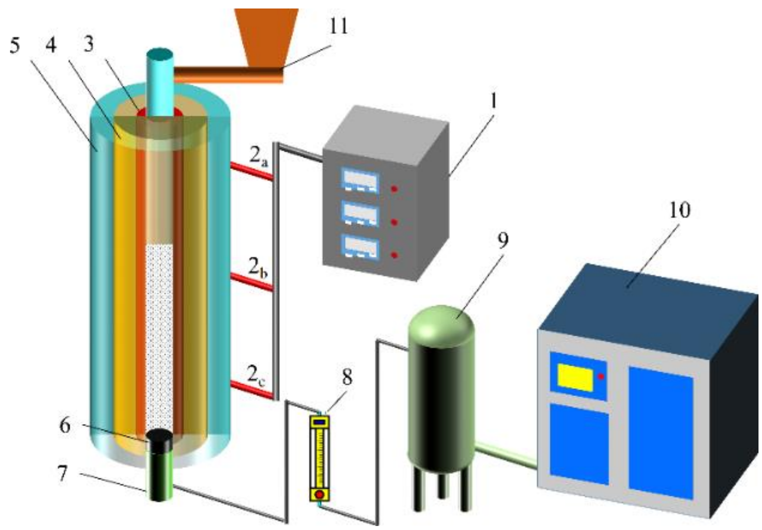

Fig. 1. Schematic of FB experimental setup: 1. Digital adjustment device, 2. Thermocouple, 3. Resistance wire, 4. Refractories, 5. Insulation material, 6. Air distribution plate, 7. Air chamber, 8. Rotameter, 9. Steady pressure jar, 10. Air compressor, 11. Screw feeder

Cement

Table 2 shows the physical and chemical properties of the Ordinary Portland Cement (OPC) used in the work. This type of OPC 42.5 was manufactured by Harbin Cement Co., Ltd. in China. The data will help to interpret the results of the subsequent tests and experiments.

Table 2. Physical and Chemical Properties of Cement

Project		Values	Project		Values
Specific Surface Area (m²/kg)		≧ 300	Chemical Ingredients (%)	Si	11.23
Initial Setting Time (min)		≧ 45		Fe	1.76
Specific Gravity (g/cm³)		3.00 ~ 3.15		Al	4.63
Compressive Strength (MPa)	3 days	≧ 17.00		Ca	37.95
	28 days	≧ 42.50		Mg	2.69
Flexural Strength (MPa)	3 days	≧ 3.50		S	1.30
	28 days	≧ 6.50		Na	0.16

Aggregates

In this study, the standard sand was prepared in accordance with the guidelines specified in GB 178-1997 (1979). Aggregates size distribution (Alrubaie *et al.* 2023) is shown in Table 3. The silicon oxide content in standard-sand was greater than 96%, the percentage of the loss of ignition (LOI) was less than 0.4%, and sediment percentage was less than 0.2%.

Table 3. Aggregates Size Distribution

Sieve Size (mm)	Cumulative Passing (%)
0.65	⩾ 97
0.40	60±5
0.25	⩽ 6

Mortar Sample

The control mixture for OPC mortar was prepared in a ratio of 1:3:0.5 of cement, standard sand, and water, respectively, in accordance with the specifications outlined in China's GB/T 17671-1999 (1999) standard. To evaluate the impact of five different types of DSLA on the strength of the mortar as cement additives, mortars containing 10% of the DSLA as a replacement for cement by weight were prepared. The value is the preferred for RHA (Bie *et al*. 2015). The composition of the mortars is presented in Table 4.

Table 4. Mortar Mixture Proportions

Mixture Name	OPC (g)	DSLA (g)	Water (mL)	Sand (g)
Control sample	450	-	225	1350
DSLA sample	405	45	225	1350

To measure the strength of both the control sample and DSLA mortar mixtures, prismatic specimens with dimensions of 40 × 40 × 160 mm^3 were prepared. After 24 h, the specimens were removed from the mold and stored in a humidity cabinet under conditions of 65% relative humidity and a temperature of 20 ± 2 °C until 3, 7, and 28 days for testing.

Methods

The SEM observations provided insight into the microstructure and surface characteristics of the DSL and DSLA samples. The SEM images were used to identify any morphological changes or structural degradation that could be due to the high temperature exposure during the treatment process. Additionally, EDX microanalysis could be used to determine the elemental composition of the samples, which can provide important information about the chemical composition and distribution of elements in the samples. Thus, SEM and EDX examinations were conducted using a SEM microscope (S-570, HITACHI, Tokyo, Japan) with a thin gold film of 10 to 20 nm thickness sputtered onto the samples. The electron micrographs were obtained at 30 kV.

The crystal structure of different DSLA samples were determined using XRD tests performed on a Rigaku D/max-r B type rotatory anode harrow X-ray diffractometer (Rigaku Corporation, Tokyo, Japan). The specific surface area of the samples was determined using a single-point Brunauer-Emmett-Teller method with a Nitrogen Adsorption Specific Surface Area Tester (3H-2000BET-A, Hui Hai Hong Nano-ST Co., Ltd., Beijing, China).

The flexural and compressive strength of the mortar mixtures were tested using an automatic constant bending stress of cement compression and flexural test machine (YAW-300C, Ji'nan Zhong Lu Chang Testing Machine Make Co., Ltd., Jinan, China) in accordance with the standard of JC/T 724-1982 (1996) with an accuracy of 1%. During compressive and flexural strength tests, the loading rates were 2400 and 50 N/s, respectively. The tests were conducted at the ages of 3, 7, and 28 days, and the reported flexural and compressive strengths were the averages of three and six samples, respectively (Bie *et al.* 2015).

RESULTS AND DISCUSSION

SEM/EDX of DSL

The comparison between the SEM images of dry rice husk and DSL highlighted the morphological differences between the two materials and provides a reference for the changes in the fiber reinforcement of the DSL. Figure 2 shows the SEM photos of dry rice husk and Fig. 3 shows the SEM images of the micro-morphologies in different sections (contour, outer surface, inner surface, cross-section) at different magnifications (×20, ×200, and ×1000). It can be seen from Fig. 3a that the main component of dry DSL was rice husk. Figures 3b and 3c describe the outer and inner surfaces of DSL, revealing that the fibers of the outer surface were fractured and both the outer and inner surfaces were covered with particles and impurities. In contrast, Fig. 3d shows that the rice husk of DSL retained the micro-characteristics of raw dry rice husk. As observed, there were numerous micro-cellular pores in DSL, and a reticular honeycomb structure, characterized by 5 μm pores, can also be seen. This structure, mainly composed of protein, sugar, lignin, cellulose, and some metallic oxide (Ouyang 2003; Bie *et al.* 2015), remained unchanged and did disappear during the fermentation process.

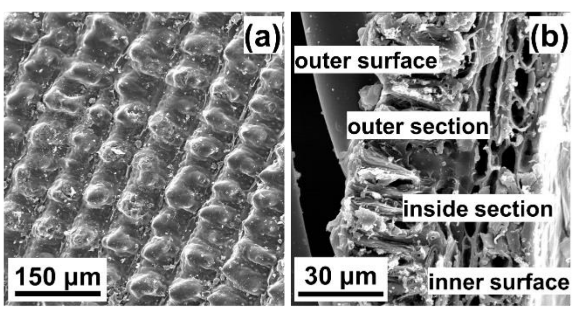

Fig. 2. SEM of dry raw rice husk: (a) outer surface, (b) cross-section

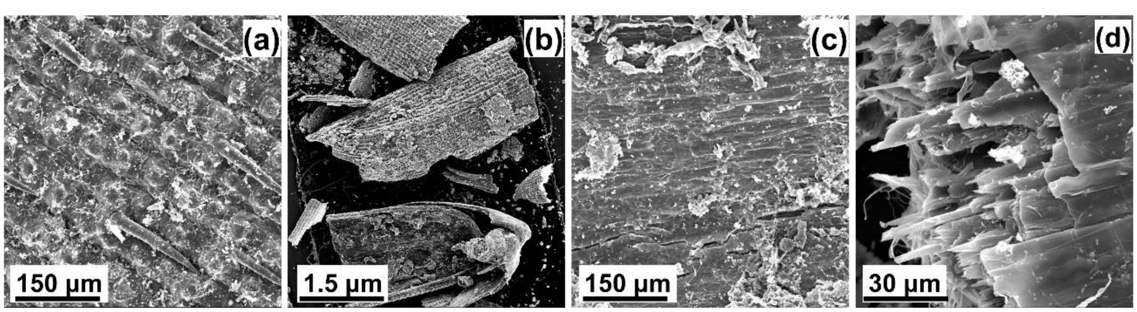

Fig. 3. SEM of dry DSL: (a) contour, (b) outer surface, (c) inner surface, and (d) cross-section

Main element contents of dry rice husk and DSL tested by EDX are shown in Table 5. As shown, the Si contents on the inner surface, outer surface, and cross-section of DSL were almost the same as that of the raw rice husk. In addition to Si, other elements, such as K, Ca, and Fe, were also found in the DSL. The fermentation process was completed in a highly acidic environment, which was equivalent to the indirect acid treatment of rice husk. This can directly explain the reason for the low thermal sensitivity of DSL. However, at the same time, the content of K on the inner surface and cross-section was much higher than that of ordinary rice husks.

Table 5. Main Element Contents of DSL and Rice Husk

Element	DSL			Rice Husk		
	Outer Surface (%)	Inner Surface (%)	Cross-section (%)	Outer Surface (%)	Inner Surface (%)	Cross-section (%)
Si	98.3657	92.0720	75.1586	97.4480	93.445	81.3033
K	0.8099	5.4270	21.0302	2.5520	3.5572	15.9446
Ca	0	1.8335	1.7588	0	2.5622	1.9159
Fe	0.4407	0.6675	2.0524	0	0.4356	0.8362
Al	0.2647	0	0	0	0	0

XRD

As shown in Fig. 4, the XRD results of the various DSLA samples demonstrate that there were no apparent peaks in the intensity curves of SiO_2. This suggests that the SiO_2 was amorphous (Maddalena *et al.* 2019), and the DSLA samples might have a pozzolanic effect and could potentially be introduced as cement additives to improve mortar strength. However, it was necessary to conduct strength tests to confirm this potential benefit.

The Specific Surface Areas

The results of the specific surface area tests are presented in Fig. 5. As shown, the specific surface area of DSLA produced in MF was higher than those produced in FB, when measured at the same temperature. Additionally, within the same furnace type, the specific surface area decreased as the temperature increased.

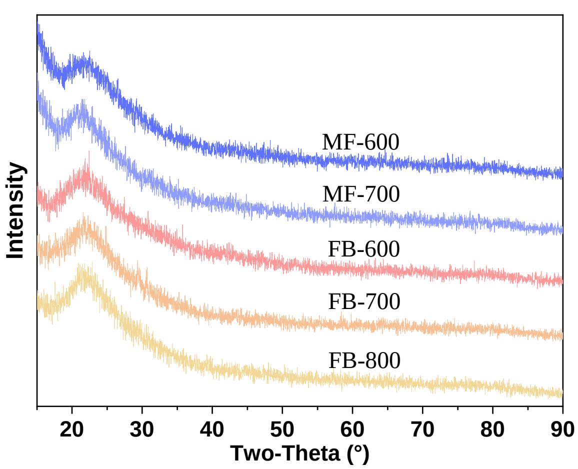

Fig. 4. XRD analysis of DSLA samples

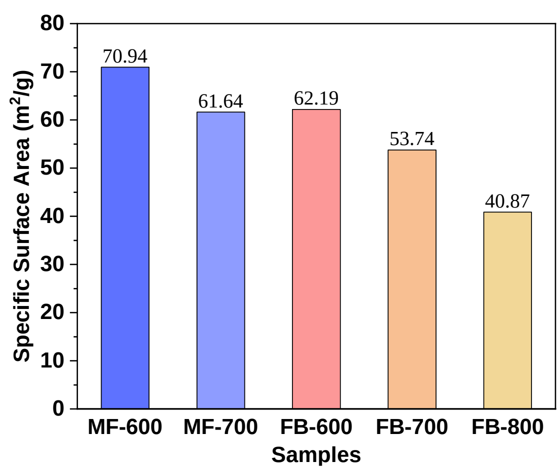

Fig. 5. The specific surface areas of DSLA

SEM of DSLA

Figure 6 displays the SEM images of DSLA obtained through MF. As evident from Fig. 6a and 6b, when DSL burned out, the shells with a high content of SiO_2 were cast off, and the internal porous structure was revealed due to the separation of volatile matter and combustion of carbon. At increased magnification, many microcellular pores were visible of 1 to approximately 5 μm (Fig. 6c and 6d). Moreover, there were also numerous granular particulates on the crisscross mesh sheets. However, unlike MF-600, some of the surfaces of the crisscross mesh sheets in MF-700 had become glazed, resulting in a lower specific surface area of MF-700 (61.64 m^2/g) compared to MF-600 (70.94 m^2/g) shown in Fig. 5.

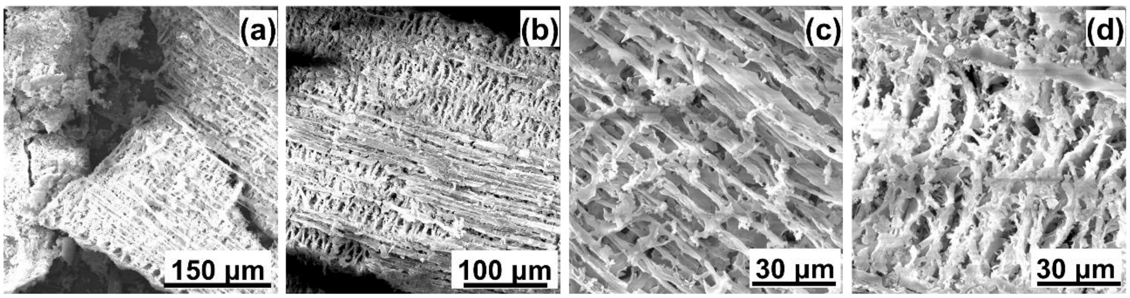

Fig. 6. SEM of DSLA obtained in MF: (a) and (c) MF-600, (b) and (d) MF-700

Figure 7 presents the SEM images of the DSLA produced through FB at temperatures of 600 °C, 700 °C, and 800 °C. Some of the shells containing high amounts of SiO_2 were shed when DSL was burned in FB. At small magnification, the three types of DSLA were quite similar (Fig. 7a through 7c). However, at larger magnification, the crisscross mesh sheets were more easily discernible and display some differences from each other (Fig. 7d through 7f). FB-600 had a higher number of granular particles than FB-700 and FB-800. In addition, the majority of crisscross mesh sheets in FB-800 had a glazed appearance. In terms of specific surface area, the values were in the order of FB-600 > FB-700 > FB-800 (Fig. 5). Referring to the specific surface area results, it was found that the number of granular particles on the sheets and the degree of glazing both play a critical role in determining the specific surface area, which increased with more granular particles matter and decreased with more glazing.

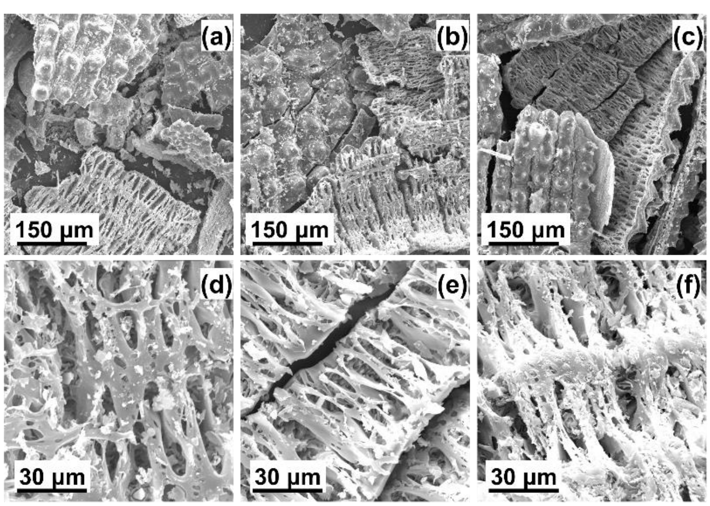

Fig. 7. SEM of DSLA in FB: (a) and (d) FB-600, (b) and (e) FB-700, and (c) and (f) FB-800

Compressive and Flexural Strength

Compressive and flexural strength data of DSLA blended mortar are shown in Fig. 8. As shown in Fig. 8a, at 3 days, only compressive strength of MF-600 was higher than the control sample. At 7 and 28 days, only the compressive strength of FB-800 was lower than the control sample. Additionally, at 28 days MF-600 and FB-600 samples were 1.17 and 1.15 times control sample, respectively. In Fig. 8b at 3 days, it can be seen that only the flexural strengths of FB-600 and FB-800 were lower than the control sample, which had the same value of 4.7 MPa. At 7 days, only the flexural strength of MF-700 was lower than the control sample. At 28 days, only the flexural strength of FB-800 was lower than the control sample. Both the compressive and flexural strengths of the MF-600's were the highest. This means that the optimal condition for producing DLSA as a cement additive is to use MF at 600 °C, which is the same as RHA results (Bie *et al.* 2015). The MF-600 can increase both compressive and flexural strengths by approximately 20%.

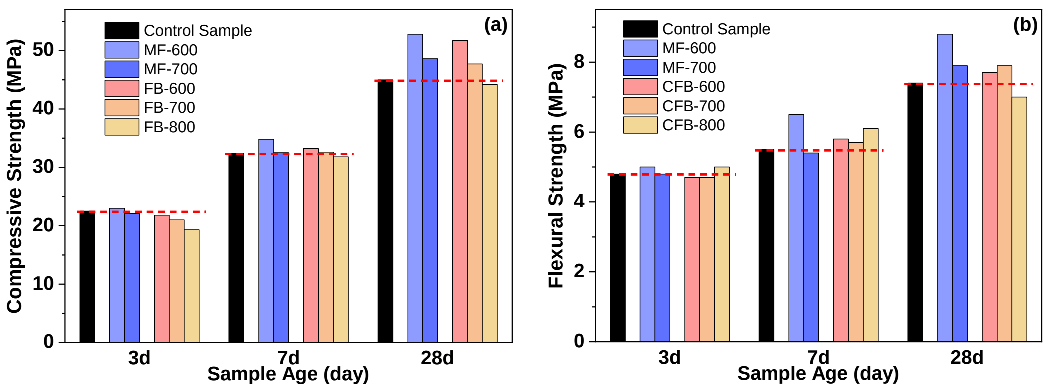

Fig. 8. Column charts of strength tests: (a) compressive strength, (b) flexural strength

Overall, the compressive strength of the mortars blended with DSLA produced in the same furnace decreased as the temperature of DSLA production increased. The flexural strength of mortars blended with DSLA produced in the MF furnace exhibited a similar trend as the compressive strength results. The strengths of the mortar blended with DSLA show improved results compared to the control samples. This improvement can be attributed to the synergistic effect between the mortar and DSLA (Isaia *et al.* 2003). The MF-600 had the best additive result, as it not only shortened the solidification time but also enhanced the ultimate compressive and flexural strengths of the mortar. Despite not reducing the solidification time, the FB-600 additive still managed to improve the ultimate strengths of the mortar. After weighing both the additive effect and the production process of DSLA, it can be concluded that combusting the DSL in FB at 600 °C was the optimal method for obtaining DSLA in this work, and that it can serve as a viable replacement for traditional blending components in cement production.

CONCLUSIONS

1. The micromorphology of rice husk in distilled spirits lees (DSL) was found to be similar to that of raw rice husk, and the unique honeycomb mesh structure of DSL was preserved during the fermentation process. The specific surface areas of the five types of DSLA were in the order of MF-600 > FB-600 > MF-700 > FB-700 > FB-800, and

the specific surface area increased with the number of granular particles and decreased with the degree of sheet surface glazing.

2. Replacing 10% of the cement with DSLA under controlled conditions led to an improvement in ultimate compressive and flexural strength, with MF-600 having the best effect as an additive.
3. This work demonstrates that the incorporation of DSLA blended in the mortar enhances its strength, making it a desirable material for various construction applications. Additionally, to achieve the industrialization of DSLA as an additive, incinerating DSL in FB at 600 °C is suggested as a practical solution.

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