COMBUSTION BEHAVIOURS OF LIGNIN-LEAN BLACK LIQUOR AND LIGNIN

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ABSTRACT

For kraft pulp mills where recovery boilers are thermally-limited, lignin removal from black liquor has become an attractive process option for increasing pulp production by allowing more black liquor to be processed through the boiler. This study systematically examined the combustion behaviours of lignin-lean black liquor and precipitated lignin from three kraft mills using a thermogravimetric (TG) combustor. The results show that adding lignin-lean black liquor to its original black liquor decreased the heating value and the degree of swelling of the mixed liquor. The effect on swelling, however, was insignificant for mixed liquors that contained less than 20% lignin-lean black liquor on a dry basis. This implies that for a given mill, up to 20% of black liquor could be treated to extract lignin without altering the burning behaviour of black liquor. As with black liquor, the combustion of lignin was found to occur through 3 main stages: drying, volatile burning and char burning. During the volatile burning stage, hardwood (HW) lignin swelled significantly, softwood (SW) lignin did not swell much, while mixed HW/SW lignin was somewhere in between. Lignin that swelled more burned more quickly than lignin that swelled less. Although the char content in lignin was about half of the volatile content, it took 10 times longer for the char to burn compared to the volatiles.

INTRODUCTION

Wood consists typically of cellulose, hemicellulose, lignin, and extractives [1]. In the kraft pulping process, lignin and most of the hemicellulose are chemically dissolved and together with spent pulping chemicals end up in the spent pulping liquor (black liquor). In order for the process to be viable, the spent pulping chemicals must be recovered and reused, which is attained by concentrating the black liquor, burning the concentrated black liquor in a recovery boiler and processing the combustion residue in the chemical recovery plant. Since the heat load on the recovery boiler is directly proportional to the lignin content in the black liquor, lignin reduction/removal from black liquor can be an attractive option for kraft pulp mills to increase their pulp production capacity by burning more lignin-lean black liquor, that has a lower heating value, in recovery boilers [2-7]. Furthermore, since the separated lignin has a high heating value, it may be used as an alternative fuel for lime kilns and power boilers [8-10].

The basic process to recover lignin from kraft black liquor has been known for many years; an acidifying agent is added to the black liquor which precipitates lignin, followed by filtration, washing and drying of the solid product. There are different commercial systems for producing lignin from kraft black liquor which follow this methodology. FPInnovations has developed improvements to the basic process, resulting in an efficient, low capital system producing high purity lignin from kraft black liquor. In this patent pending process, the black liquor is oxidized under controlled conditions before the acidification step. The oxidation improves the filterability of the precipitated lignin by providing suitable conditions for lignin colloid agglomeration. Oxidation also minimizes total reduced sulfur (TRS) compounds, leading to minimal TRS emissions during all steps associated with lignin precipitation, filtration and washing. Furthermore, since the oxidation of TRS compounds and sugars consumes alkali in black liquor, the CO_2 and sulfuric acid requirements of the process are significantly reduced [6,7].

Figure 1 shows a simple flow diagram of the kraft lignin removal process. A side stream of black liquor with a solids content of about 30% is taken from the black liquor evaporation plant and treated in a lignin reactor to extract lignin by acidifying the liquor with carbon dioxide (CO_2). The resulting slurry from the lignin reactor is sent to a filter press, where the precipitated lignin is separated from the liquor and then washed with sulfuric acid and water to purify the lignin. The liquor filtrate (known also as lignin-lean black liquor) is returned along with the lignin wash filtrate to either the weak black liquor tank or to the evaporation plant and mixed with the regular main stream black liquor, and further concentrated and fired in the recovery boiler [6,7].

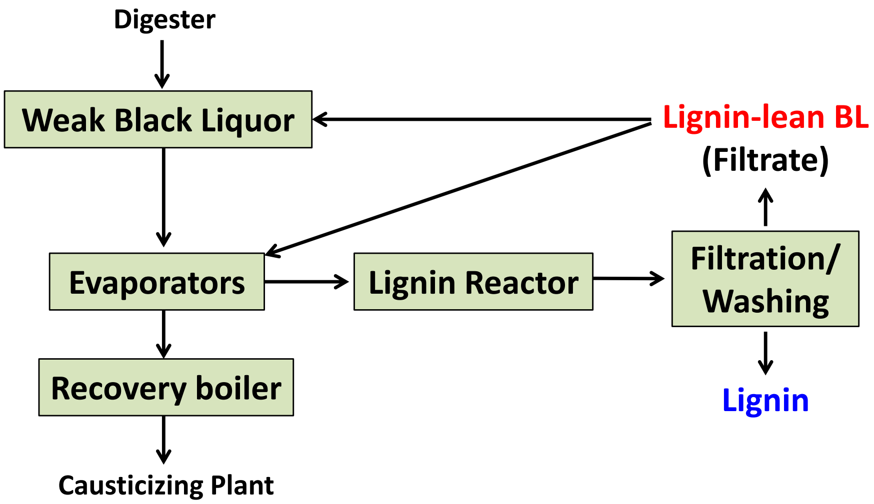

Figure 1. *Integration of lignin removal in the kraft recovery process*

It is not well understood if the lignin-lean black liquor returned to the process has an impact on the combustion of the mixed liquor in recovery boilers, what the combustion behaviour of the precipitated lignin is, and how the combustion behaviour of lignin might be valuable for burning in lime kilns and power boilers. The objectives of this research project were to i) examine the effect of lignin-lean black liquor on the combustibility of mixed liquor, and ii) systematically investigate the combustion characteristics of various types of lignin samples.

THE EXPERIMENTS

Black Liquors and Lignin-lean Black Liquors

To study the effect of lignin-lean black liquor on liquor combustibility, two weak black liquors, one from softwood and one from hardwood, and their corresponding lignin-lean black liquors were used. All of the tested liquor samples were obtained from a kraft pulp mill. Table 1 summarizes the wood types, wood species, solids contents, ash contents, and heating values.

Table 1. *Properties of black liquors and lignin-lean black liquors tested*

Liquor	**Wood Type**	**Wood Species**	**Solids** (wt%)	**Ash** (wt% BLDS)	**Heating Value**	
					MJ/Kg BLDS	Btu/lb BLDS
Weak BL #1	Softwood	Jack pine/spruce	31.9	39.1	12.8	5518
Lignin-lean BL #1	Softwood	Jack pine/spruce	23.5	48.4	8.4	3592
Weak BL #2	Hardwood	Aspen	26.7	42.5	12.7	5446
Lignin-lean BL #2	Hardwood	Aspen	22.7	53.5	8.1	3468

Lignin

A total of 9 lignin samples were investigated in this study, including 7 lignin samples from 3 kraft pulp mills and 2 commercial lignin samples. Table 2 summarizes the wood types, wood species, solids contents, heating values, and compositions of these lignin samples. Samples are labeled as A, B, C, etc., followed by a number. For example, lignin samples A1–A5 are from Mill A, but collected under different operating or processing conditions. Lignin B has no number meaning that it is the only sample received from Mill B.

Table 2. *Properties of lignin tested*

Lignin	**Wood Type**	**Wood Species**	**Solids** (wt%)	**Heating Value**		**Water** (wt%)	**Volatile** (wt%)	**Char** (wt%)	**Ash** (wt%)
				MJ/Kg DS	Btu/lb DS				
A1	Softwood	Jack pine/spruce	92.9	27.3	11750	7.1	61.8	28.9	2.2
A2	Softwood	Jack pine/spruce	81.0	23.1	9918	19.0	34.8	34.5	11.7
A3	Hardwood	Aspen	90.1	25.6	10985	9.9	60.2	29.1	0.8
A4	Hardwood	Aspen	81.2	20.6	8868	18.8	54.7	17.7	8.8
A5	Mixed	Jack pine, spruce/aspen	95.2	26.6	11452	4.8	61.5	31.9	1.8
B	Hardwood	Eucalyptus	43.1	22.2	9546	56.9	24.3	16.4	2.4
C	Hardwood	Commercial	100	26.6	11442	0	69.4	30.6	0*
D	Softwood	Commercial	100	26.5	11404	0	67.2	31.5	1.3
E	Softwood	Commercial	100	25.7	11056	0	52.9	46.2	0.9

**0: Not detectable*

Thermogravimetric Combustor

In order to systematically study the effect of lignin-lean black liquor on the combustibility of mixed liquor and to fairly compare the combustion behaviours of various types of lignin samples, tests need to be carried out under the same conditions. The availability of a thermogravimetric (TG) combustor in our laboratory at the University of Toronto (Figure 2) is suitable to achieve these conditions.

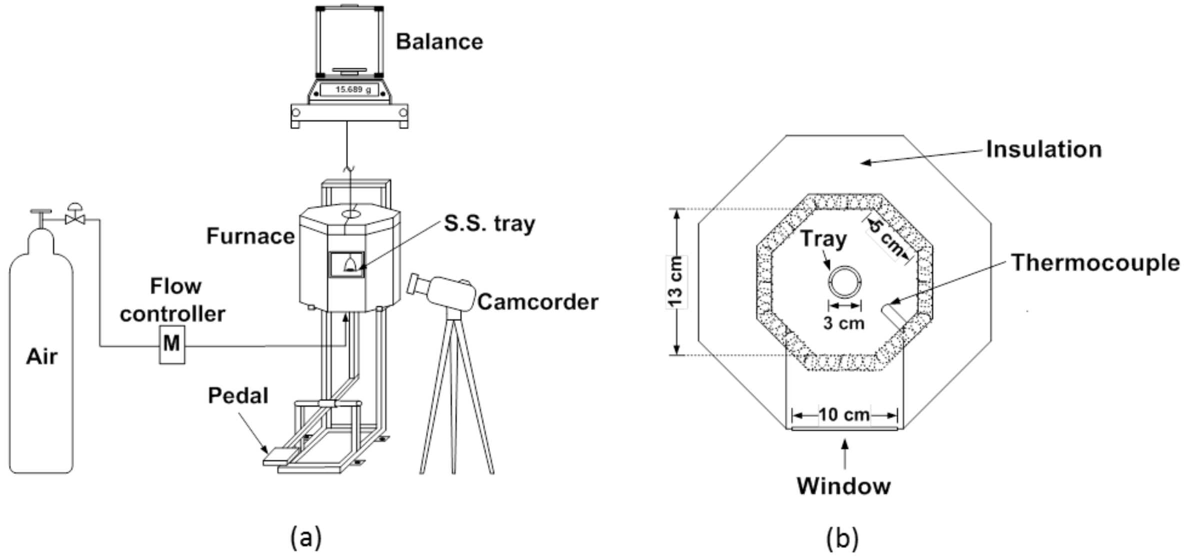

Figure 2. *a) Thermogravimetric (TG) combustor and b) Cross section of the electrical furnace [11]*

Figure 2a shows the schematic of the TG-combustor used in this study, which consists of an electrical furnace, a high precision balance, a high-definition digital camcorder and a gas control system. The electrical furnace cross section is shown in Figure 2b. The furnace has a 10 cm x 10 cm quartz glass observation window mounted on its front wall. The balance, capable of measuring up to 200 g with a readability of 1 mg, is placed on a well-insulated board directly above the furnace. The camcorder is mounted on a tripod 75 cm away from the furnace, with its lens zoomed in on the test sample in the furnace through the quartz glass window. The gas control system regulates compressed air and passes it through an air distributor at the bottom of the furnace. Details of the TG-combustor and its operating procedures have been previously described [11].

Test Procedure

All weak black liquors, lignin-lean black liquors, and their mixtures were first concentrated to about 70 wt% solids content before testing, while all lignin samples were burned as is. The furnace was controlled at 830°C, and the temperature was monitored and controlled using a K-type thermocouple placed near the test sample (Figure 2b). The liquor sample (0.3 ± 0.01 g), or the lignin sample (0.2 ± 0.01 g in dry solids mass) was placed on a stainless steel type 316 tray (3 cm O.D.) and hung on a hook underneath the balance. After the sample weight was appropriately tared and the tray became stable, the camcorder was turned on. The furnace was subsequently pushed up to quickly submerge the sample tray into the middle of the furnace. The sample appearance was recorded by the camcorder through the glass window, while the sample weight was continuously recorded by the balance. During the test, the air flow was controlled at 1L/min.

The time required for each combustion stage was determined based on video images recorded by the camcorder and the weight loss registered by the balance. The swelling of the sample was measured from the two-dimensional image of the sample at the time when its swollen volume reached a maximum.

RESULTS AND DISCUSSION

Effect of Lignin-lean Black Liquor on Liquor Combustibility

In order to examine the effect of lignin-lean black liquor on the combustion behaviour of mixed liquor, two weak black liquor samples (one softwood black liquor and one hardwood black liquor) were mixed with various amounts of their corresponding lignin-lean black liquors. The mixture was uniformly mixed and concentrated to a solids content of 70 wt% prior to burning in the TG-combustor.

In Figure 3, the maximum swelling of softwood and hardwood liquors was plotted against the lignin-lean liquor content. Maximum swelling is defined as the maximum swollen volume of the sample during the test per mass of initial sample dry solids, and is expressed as cm^3/g ds. The amount of lignin-lean black liquor mixed with the regular black liquor is expressed as wt% lignin-lean liquor dry solids (ds). In the graph, for the regular black liquor (0 wt% lignin-lean liquor content), the measured maximum swollen volume was about 32 cm^3/g ds for the softwood liquor and 34 cm^3/g ds for the hardwood liquor. For softwood and hardwood lignin-lean black liquor (100 wt% lignin-lean liquor content), the maximum swelling was about 9 cm^3/g ds. The results suggest that no significant difference in the maximum swelling was observed between softwood black liquor and hardwood black liquor, as well as between their corresponding lignin-lean black liquors. As the lignin-lean liquor content increased, the maximum swelling decreased for softwood liquors. A similar trend was observed for hardwood liquors, but to a lesser extent. The results for hardwood liquors are in agreement with those reported by Vähä-Savo et al. [12]. In our study, however, when the lignin-lean liquor content was below 20%, no significant change in swelling was found for softwood and hardwood liquors (Figure 3). It may be concluded that up to 20% of black liquor may be treated to extract lignin without altering the burning behaviour of black liquor.

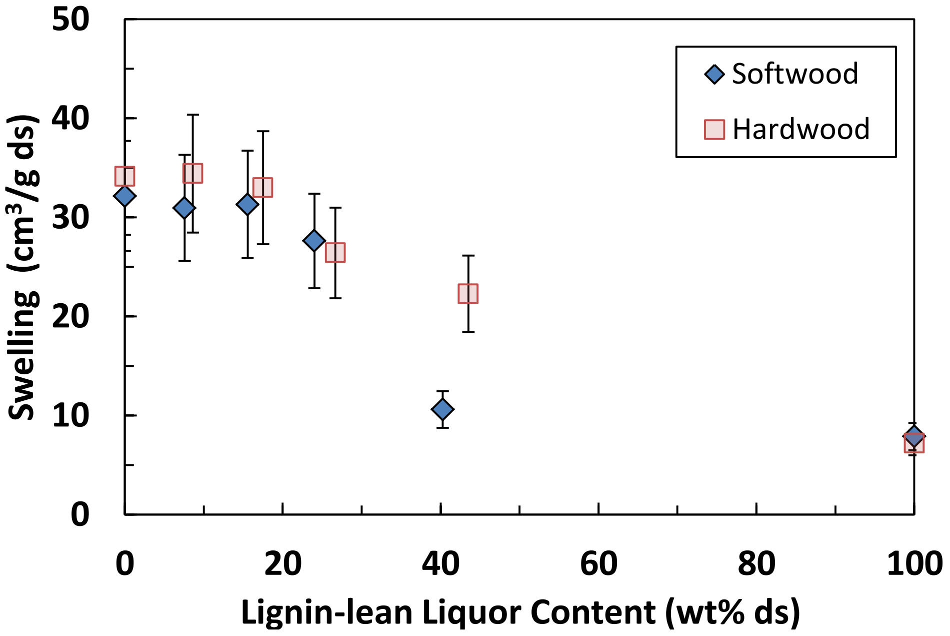

Figure 3. *Effect of lignin-lean liquor content on swelling for two liquors burned at 830°C in air*

The effect of lignin-lean black liquor on the total combustion time is shown in Figure 4 where the total combustion times are normalized as second per gram of dry solids (sec/g ds). For softwood and hardwood liquors, as lignin-lean liquor content increased, the total combustion times increased. However, little change in time was observed for liquors with lignin-lean liquor content less than 20%.

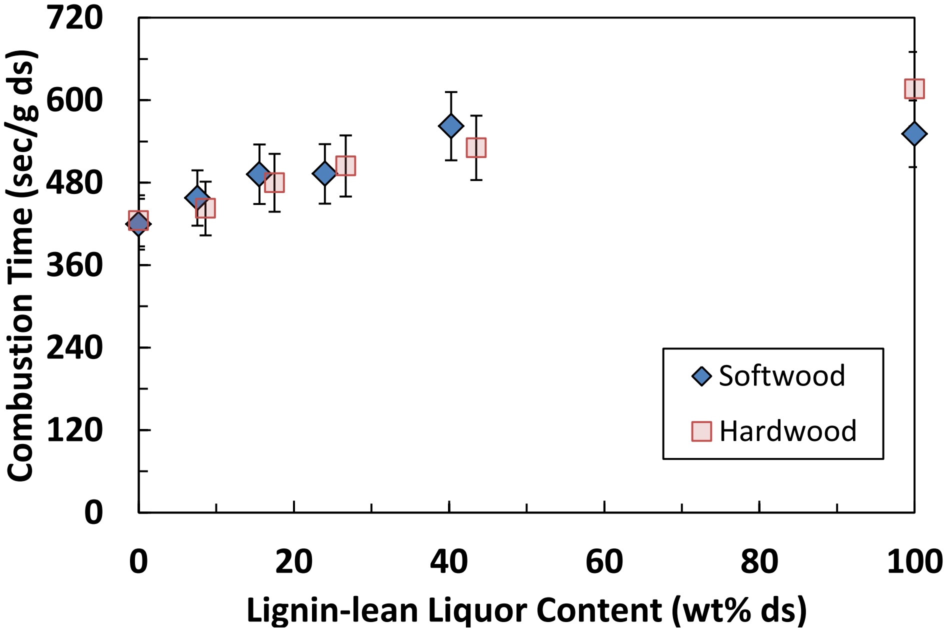

Figure 4. *Effect of lignin-lean liquor content on total combustion time for two liquors burned at 830°C in air*

Lignin Combustion Behaviour

Figure 5 shows still frames extracted from combustion test videos for lignin A1 (softwood jack pine/spruce), lignin A3 (hardwood aspen), and lignin B (hardwood eucalyptus), from the beginning (row 1) to the end (row 9).

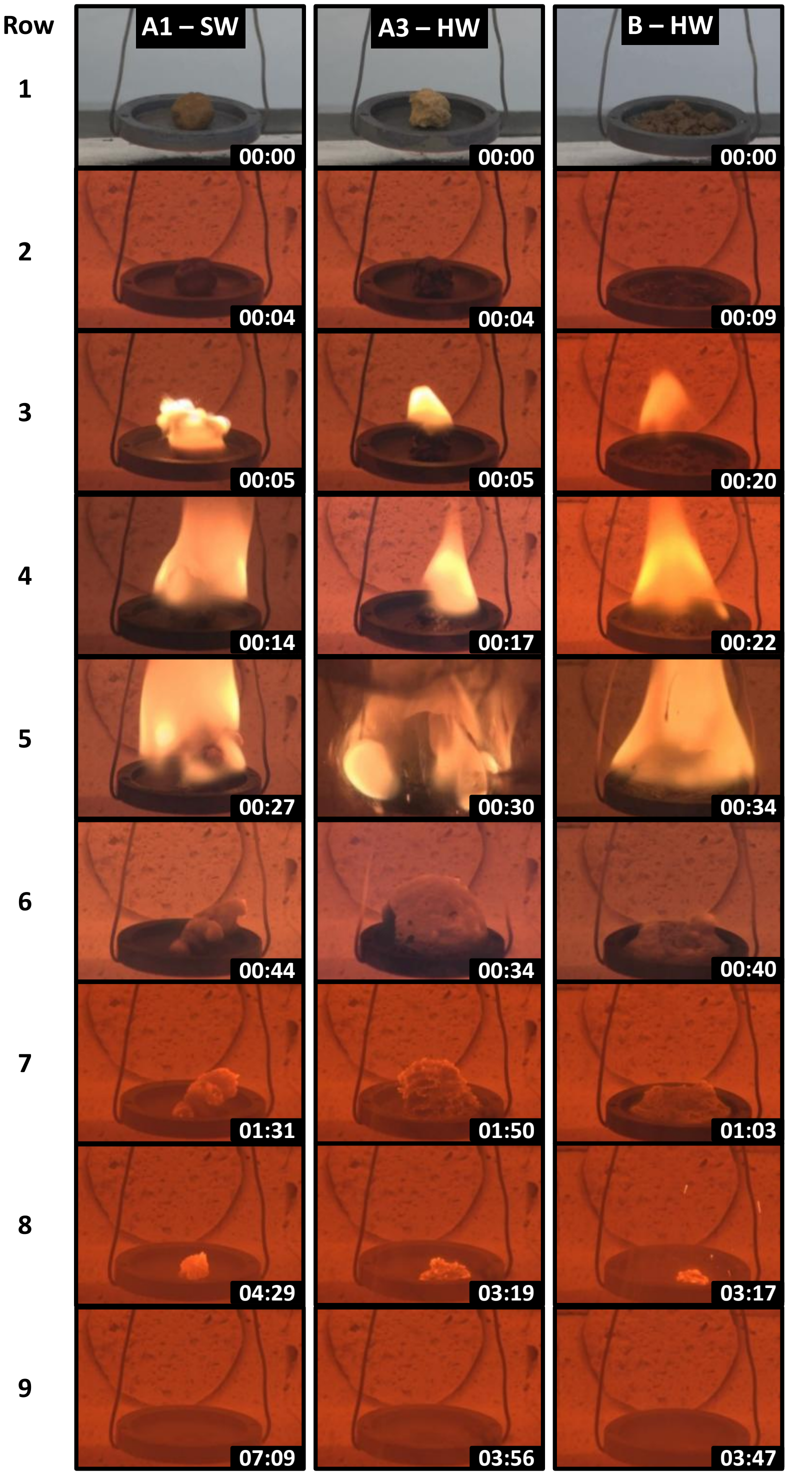

Figure 5. *Lignin A1 (softwood jack pine/spruce), lignin A3 (hardwood aspen), and lignin B (hardwood eucalyptus) combustion process at 830°C in air (time displayed in mm:ss)*

As soon as the samples were submerged in the furnace, water vaporization in the samples occurred instantly (row 2). At about 5 seconds, softwood lignin A1 and hardwood lignin A3 caught fire and formed a bright yellow flame indicating the burning of devolatilized or pyrolysis gases (row 3). On the other hand, hardwood lignin B ignited within about 20 seconds; this much longer time was due to the sample containing about 57 wt% moisture. During devolatilization (rows 3, 4 and 5), all samples burned with an intensive flame. Hardwood lignin A3 and B melted after the flame appeared (row 4), while hardwood lignin A3 also produced a large amount of smoke (row 5). In addition, all samples swelled during this stage. Hardwood lignin A3 swelled the most, followed by hardwood lignin B. Softwood lignin A1 swelled the least. The yellow flame eventually disappeared indicating the completion of the devolatilization stage, as well as the beginning of the char burning stage (row 6). For all the lignin samples tested, the char burning stage (rows 6, 7 and 8) took a much longer time to complete than the devolatilization stage.

A similar combustion behaviour (drying, devolatilization, and char burning) was observed for lignin A4 that was extracted from black liquor produced from hardwood aspen. However, its appearance during combustion was distinctive as shown in Figure 6. As the sample was introduced in the furnace, it swelled immediately following ignition. With time, the sample rolled and formed a snake-like shape. During devolatilization, the sample swelled enormously. The formation of molten smelt beads was clearly observed for this sample. This was likely because this lignin was not well washed; it still contained some black liquor and had an ash content of about 9 wt%.

Figure 6. *Lignin A4 (hardwood aspen) combustion process at 830°C in air (time displayed in mm:ss)*

Lignin Swelling

Figure 7 compares the maximum swelling of 9 lignin samples tested in this study. Maximum swelling is defined as the maximum swollen volume of the sample during the test per mass of initial lignin dry solids, and is expressed as cm^3/g ds. In this figure, softwood lignin (A2, A1, D, and E), mixed lignin (A5), and hardwood lignin (B, C, A4, and A3) are labeled. The results clearly show that softwood lignin samples exhibited the least swelling, less than 11 cm^3/g ds, while hardwood lignin samples swelled more, from 15 to 37 cm^3/g ds. The maximum swollen volume of the mixed lignin was somewhere in between, about 12 cm^3/g ds. The results are in agreement with those reported by Alén et al. [13].

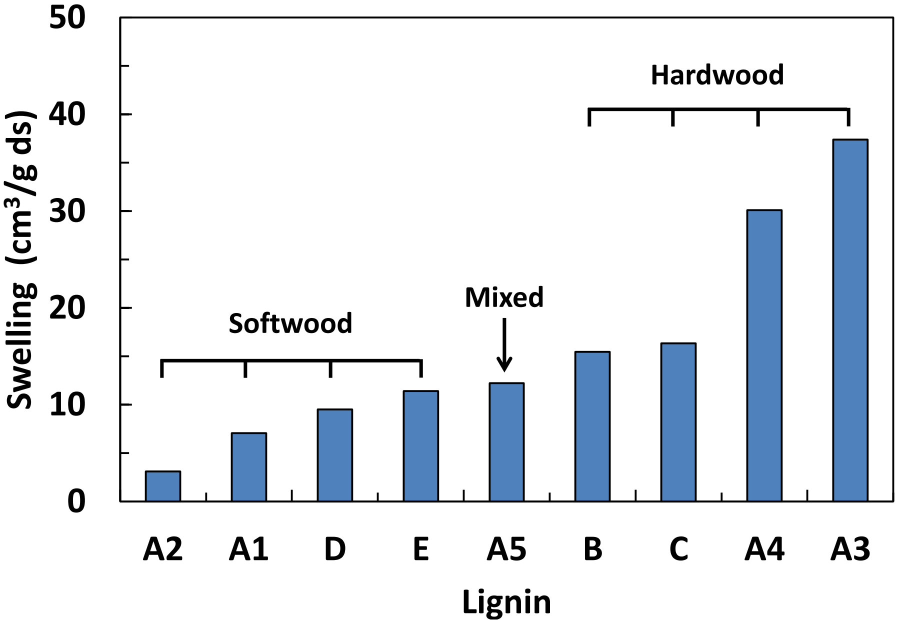

Figure 7. *Maximum swollen volumes of 9 lignin samples burned at 830°C in air*

Lignin Combustion Stages and Times

Figure 8 shows the weight change curves for all 9 lignin samples tested in this study. In this figure, only the curves for lignin A1, lignin A2, and lignin A5 are labeled with arrows. The profiles are similar. In all cases, the sample weight reduced more than 60% within the first 60 seconds due to drying and devolatilization. The weight continued to decrease, but at a lower rate, as char burning continued. Eventually the curve became relatively flat, suggesting the completion of the burning process. The total combustion time varied with lignin sample. Lignin A1, lignin A2, and lignin A5 took more than 300 seconds to complete, while the remaining lignin samples completed combustion within 240 seconds.

In theory, combustion follows 3 main stages: drying, devolatilization, and char burning; drying should occur before devolatilization, and devolatilization should complete before char burning. In this study, due to the relatively large sample size used and possible uneven temperature distribution within the sample, drying and devolatilization stages overlapped and could not be clearly distinguished. However, it was relatively easy to differentiate devolatilization from char burning because of the much slower char burning rate than devolatilization rate. Thus, the lignin combustion stages in this study were defined as time-to-ignition, volatile burning, and char burning. The time-to-ignition was used to describe the stage prior to ignition. The volatile burning stage was based on the time at which a flame first appeared to when it disappeared. The char burning stage was taken as the time from the disappearance of the flame until the completion of combustion.

Using the weight change curves shown in Figure 8 and the solids content of the samples, the volatile content, char content, and ash content of each lignin sample can be calculated. The results are summarized in Table 2. Details of the calculation procedure have been previously described [11].

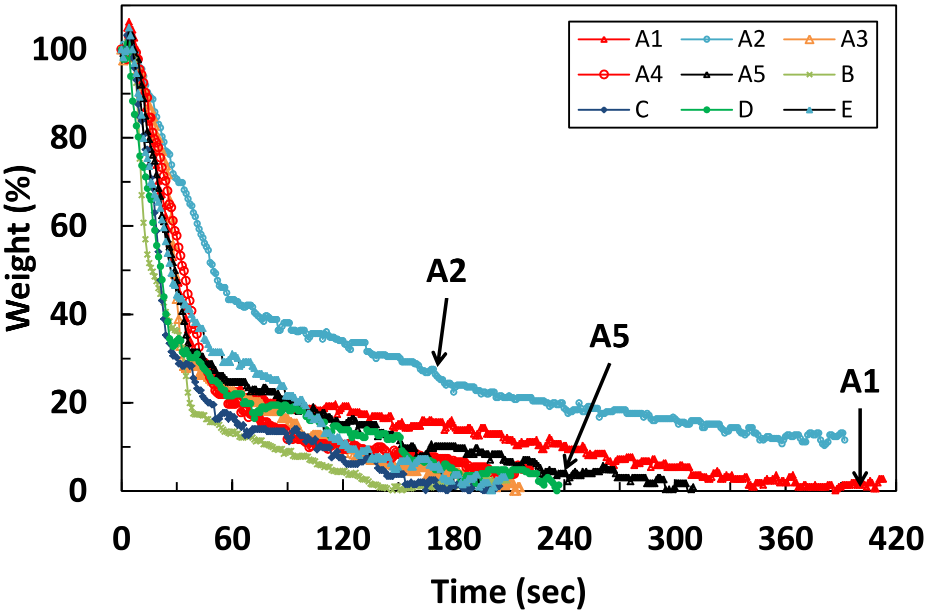

Figure 8. *Weight change profiles of 9 lignin samples with time when burned at 830°C in air*

Figure 9 shows the elapsed times for combustion stages of all lignin samples tested. Since the samples had different solids contents, the combustion stage times were normalized by the sample dry mass (sec/g ds). The time-to-ignition and volatile burning stages were much shorter than the char burning stage. In addition, the maximum swelling of each lignin sample (indicated by black dots) occurred either during volatile burning or at the point when all volatile matter had burned out.

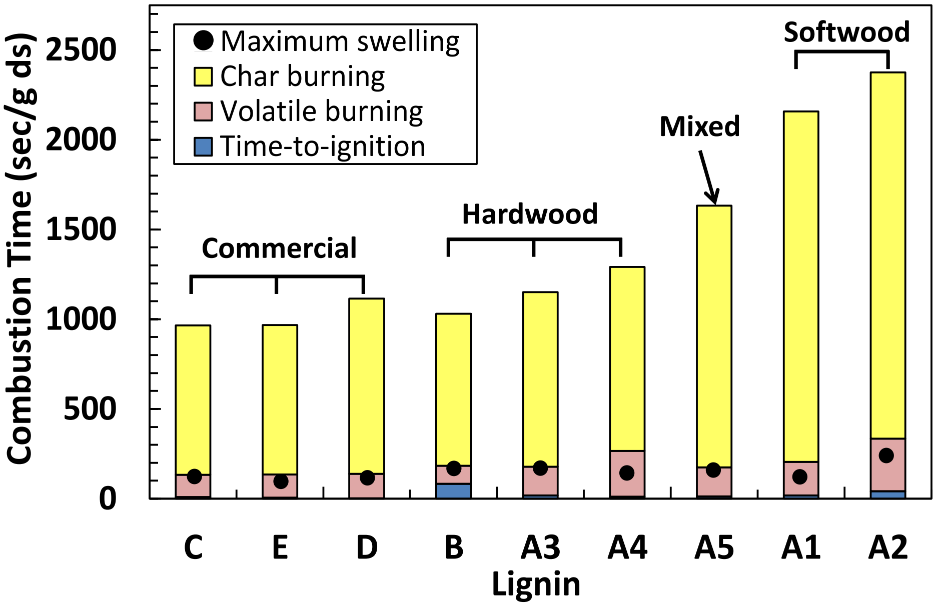

Figure 9. *Combustion times of 9 lignin samples burned at 830°C in air*

Effect of Lignin Swelling

Figure 10 plots the time required for individual combustion stages (time-to-ignition, volatile burning, and char burning) and the total combustion time as a function of the maximum swollen volume of the samples for over 50 combustion tests. In the figure, it is clearly shown that the maximum swelling had little impact on the time-to-ignition for all the lignin samples tested. This is presumably because the maximum swelling occurred way after the sample ignited (Figure 9). The volatile burning time slightly decreased as the maximum swelling increased up to about 20 cm^3/g ds, beyond which there was little change. Similarly, the char burning time and thereby the total combustion time significantly decreased as the maximum swelling increased. The results are plausible since greater swelling produces char with a higher porosity, making it easier for air to penetrate into the interior of the char thereby shortening the volatile burning and char burning times.

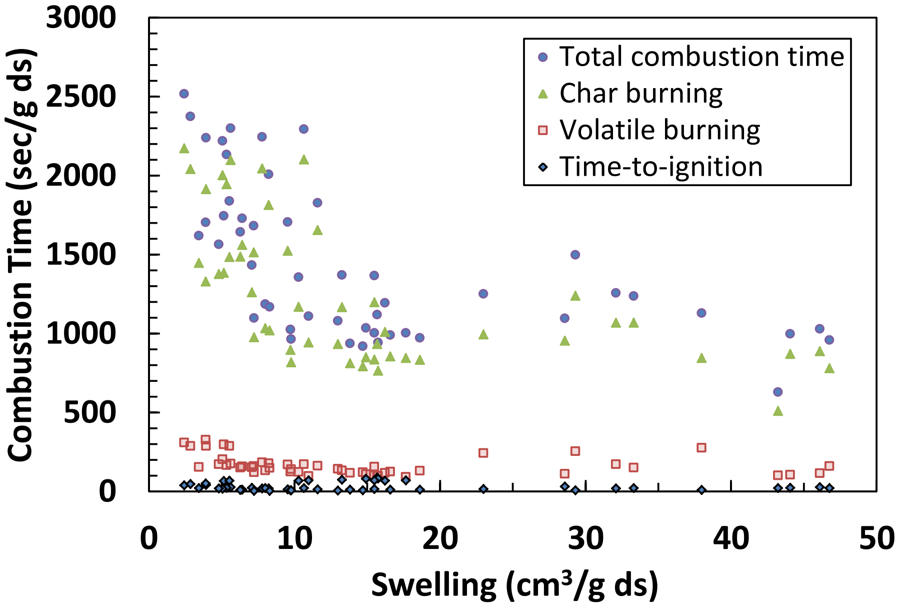

Figure 10. *Effect of swelling on combustion times for lignin samples burned at 830°C in air*

SUMMARY

A systematic study was performed to examine the combustion behaviours of lignin-lean black liquor and precipitated lignin using a thermogravimetric (TG) combustor. The results show that:

- Adding lignin-lean black liquor to its original black liquor decreased the heating value and the degree of swelling of the mixed liquor. The effect on swelling, however, was insignificant for mixed liquors that contained less than 20% lignin-lean black liquor on a dry basis. This implies that for a given mill, up to 20% of black liquor could be treated to extract lignin without altering the burning behaviour of black liquor.

- As with black liquor, the combustion behaviour of lignin was found to occur through 3 main stages: drying, volatile burning and char burning.

- During the volatile burning stage, hardwood (HW) lignin swelled significantly, softwood (SW) lignin did not swell much, while mixed HW/SW lignin was somewhere in between.

- Lignin that swelled more burned more quickly than lignin that swelled less. Although the char content in lignin was about half of the volatile content, it took 10 times longer for the char to burn compared to the volatiles.

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Combustion Behaviours of Lignin-lean Black Liquor and Lignin

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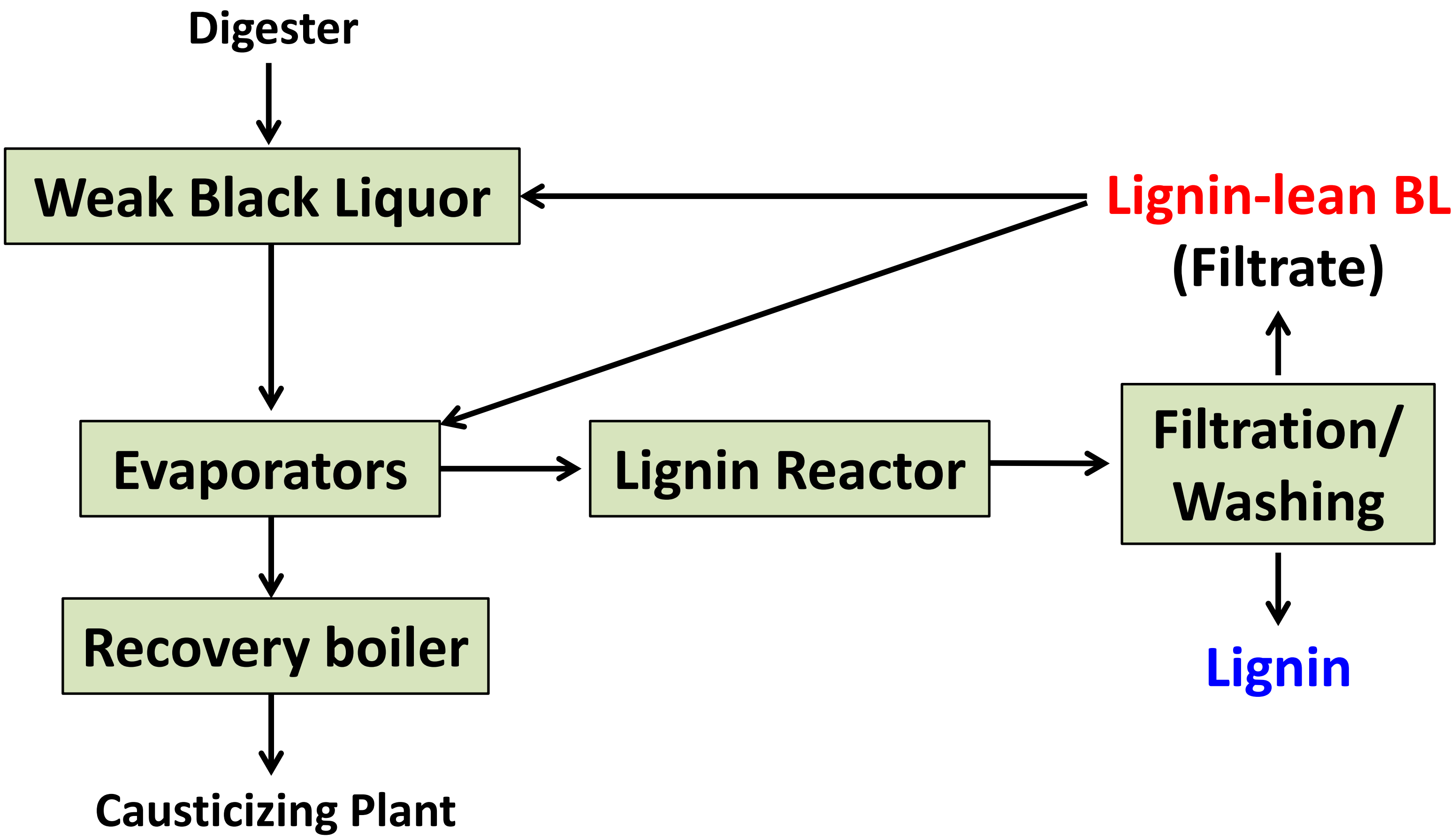
Lignin Removal

- Lignin
  - It is chemically dissolved and together with spent pulping chemicals end up in the black liquor
- Lignin removal from black liquor has become an attractive process option
  - It gives a potential to increase pulp production capacity
  - The separated lignin has a high heating value that may be used as an alternative fuel to burn in lime kilns and power boilers

Lignin Recovery Process

- **Lignin recovery methodology**
  - **Acidify black liquor to precipitate lignin**
  - **Separate solids through filtration**
  - **Wash and dry the solid product**
- **Different commercial systems are available for producing lignin from black liquor**
  - **FPInnovations has improved the basic process by oxidizing the black liquor before acidification step**
    - Improves filterability of the precipitated lignin
    - Minimizes TRS compounds
    - Reduces CO_2 and sulfuric acid consumptions

Integration of Lignin Removal Process

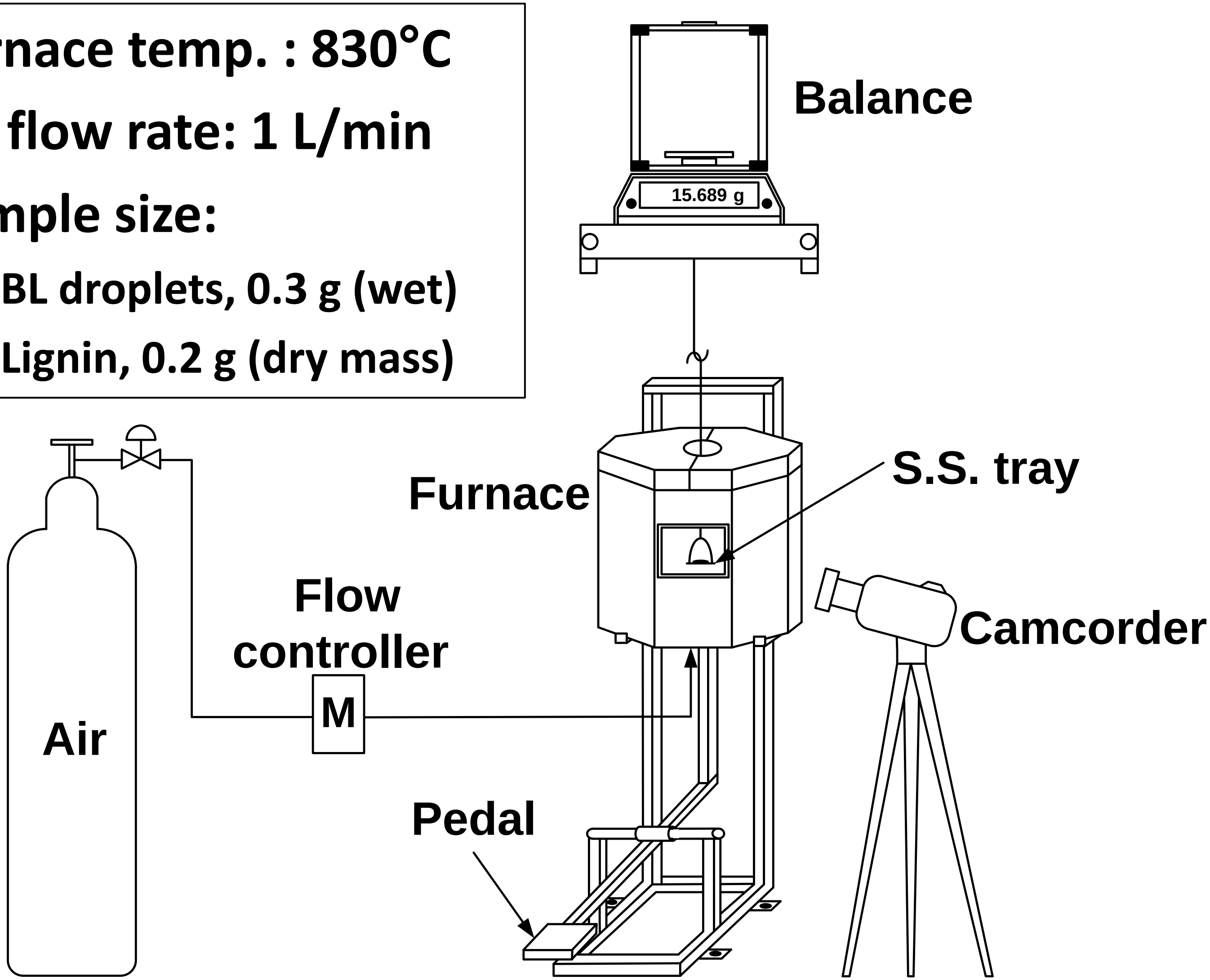


Objectives

- To examine:
  - Whether the lignin-lean black liquor returned to the process has an impact on the combustion of the mixed liquor in recovery boilers?
  - What is the combustion behaviour of the precipitated lignin?
  - How the combustion behaviour of lignin might be valuable for burning in lime kilns and power boilers?

Thermogravimetric Combustor

- Furnace temp. : 830°C
- Air flow rate: 1 L/min
- Sample size:
  - BL droplets, 0.3 g (wet)
  - Lignin, 0.2 g (dry mass)



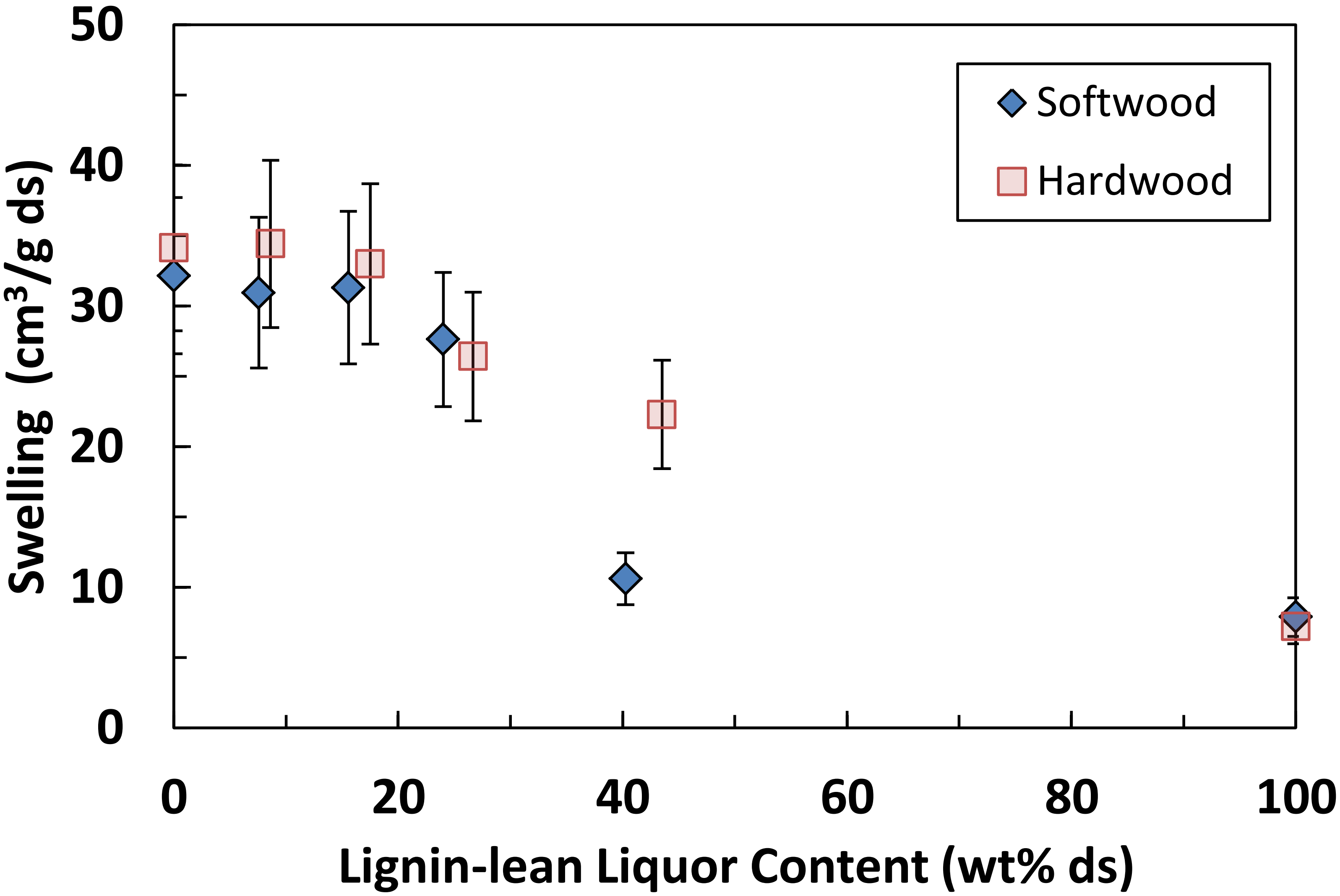
Effect of Lignin-lean BL on Combustibility

- Properties of liquors tested

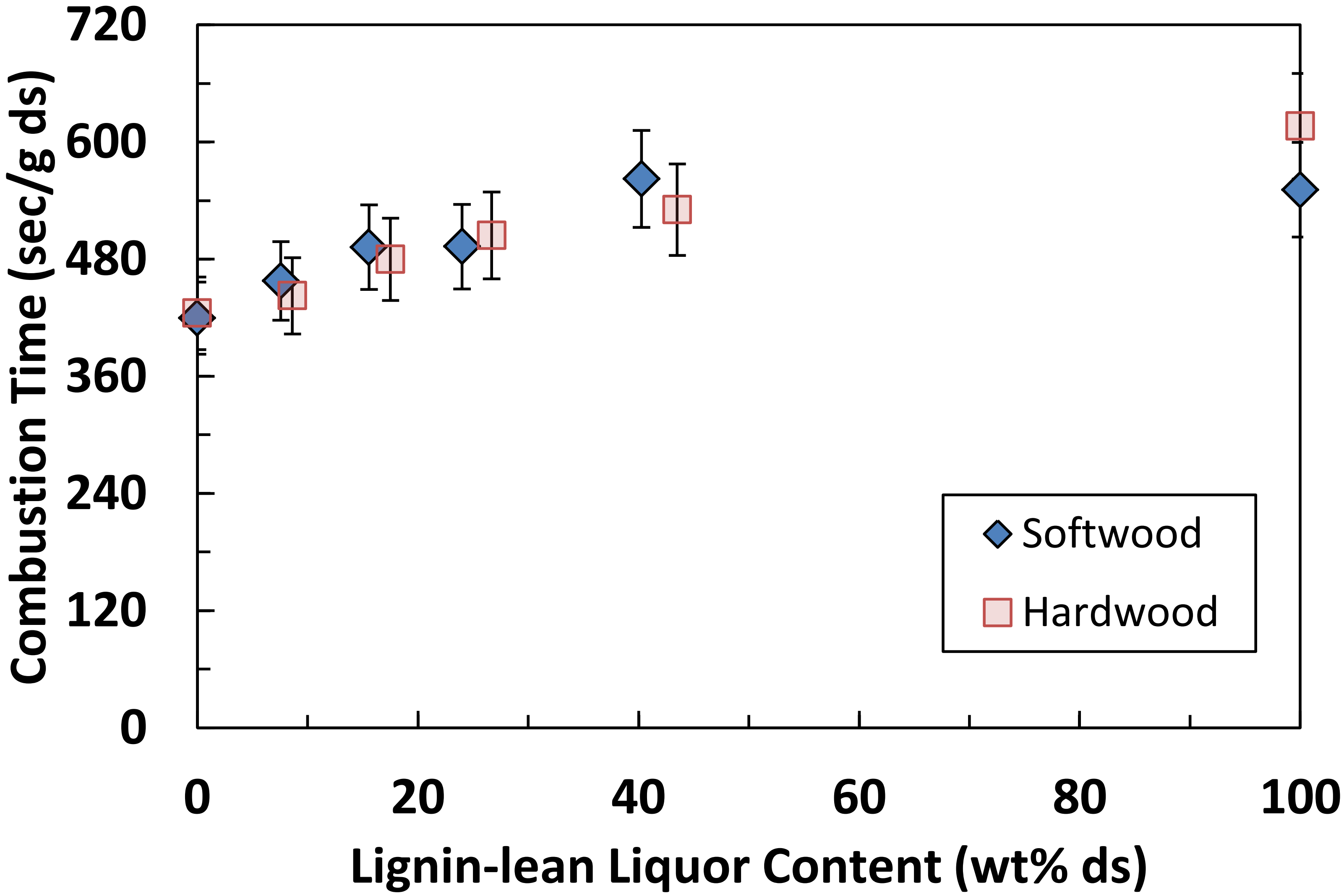
Liquor	Wood Type	Wood Species	Solids (wt%)	Ash (wt% BLDS)	Heating Value (Btu/lb BLDS)
Weak BL #1	Softwood	Jack pine/spruce	31.9	39.1	5518
Lignin-lean BL #1	Softwood	Jack pine/spruce	23.5	48.4	3592
Weak BL #2	Hardwood	Aspen	26.7	42.5	5446
Lignin-lean BL #2	Hardwood	Aspen	22.7	53.5	3468

- Sample droplets
  - Mixture of weak BL and lignin-lean BL
  - Constant solids content ~70%
  - Various amounts of lignin-lean BL

Effect of Lignin-lean BL on Swelling



Effect of Lignin-lean BL on Total Combustion Time



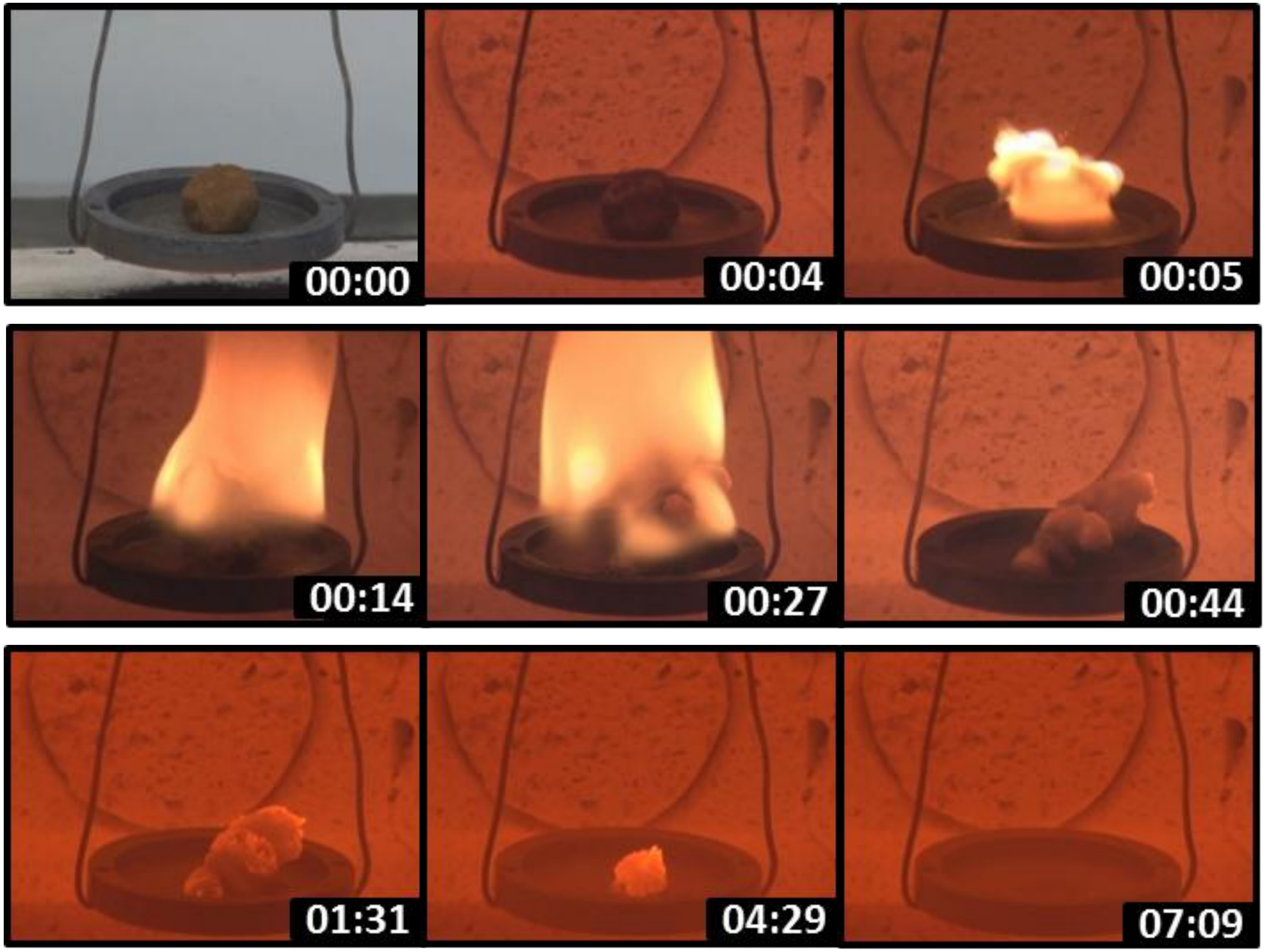
Lignin Tested

- 7 lignin samples from 3 kraft pulp mills and 2 commercial lignin samples

Lignin	Wood Type	Wood Species	Solids (wt%)	Ash (wt% DS)	Heating Value (Btu/lb DS)
A1	Softwood	Jack pine/spruce	92.9	2.4	11750
A2	Softwood	Jack pine/spruce	81.0	14.4	9918
A3	Hardwood	Aspen	90.1	1.0	10985
A4	Hardwood	Aspen	81.2	10.9	8868
A5	Mixed	Jack pine, spruce/aspen	95.2	1.9	11452
B	Hardwood	Eucalyptus	43.1	5.5	9546
C	Hardwood	Commercial	100	0.0	11442
D	Softwood	Commercial	100	1.3	11404
E	Softwood	Commercial	100	0.9	11056

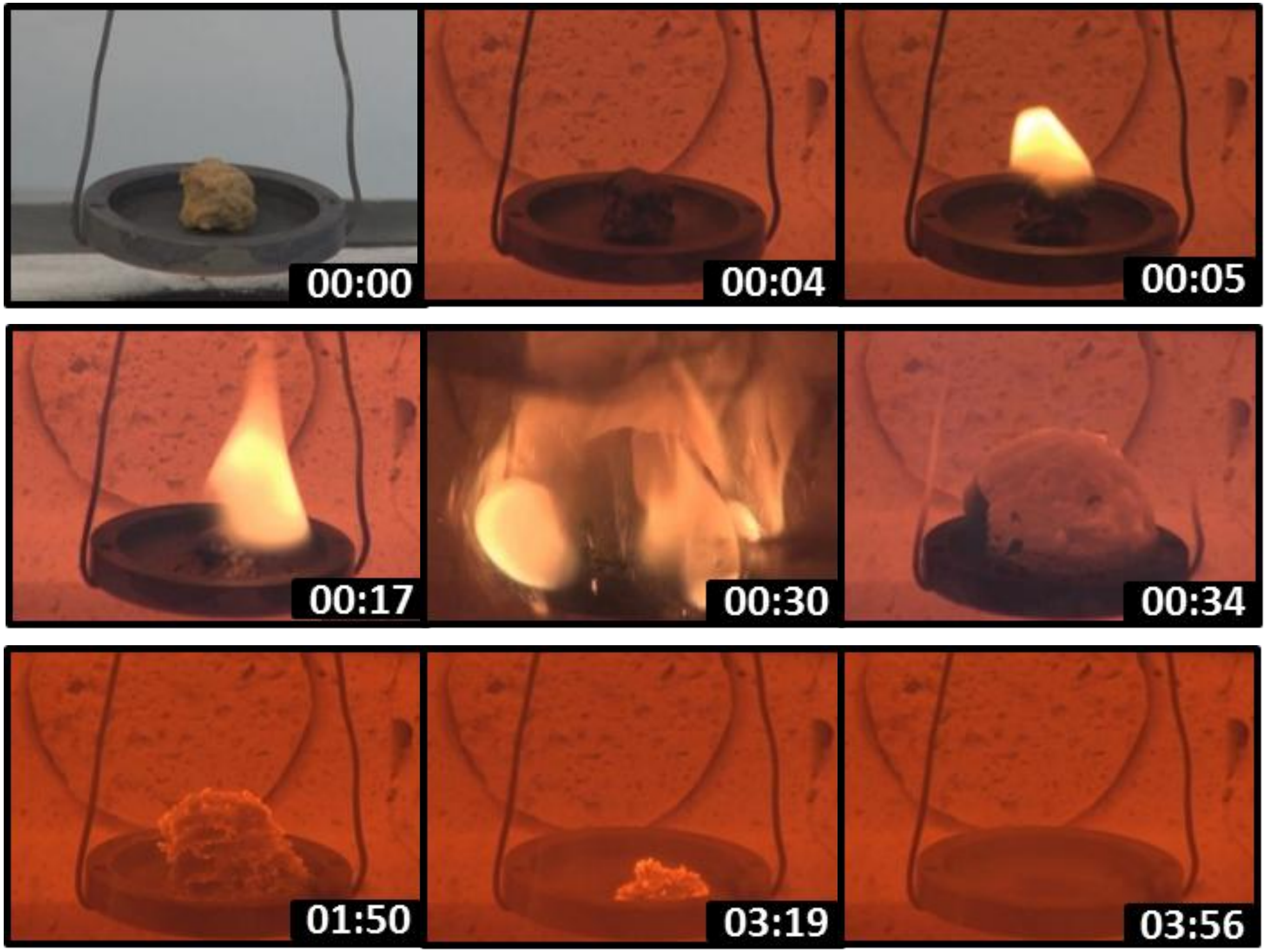
Softwood Lignin Combustion

- **Lignin A1 from jack pine/spruce**



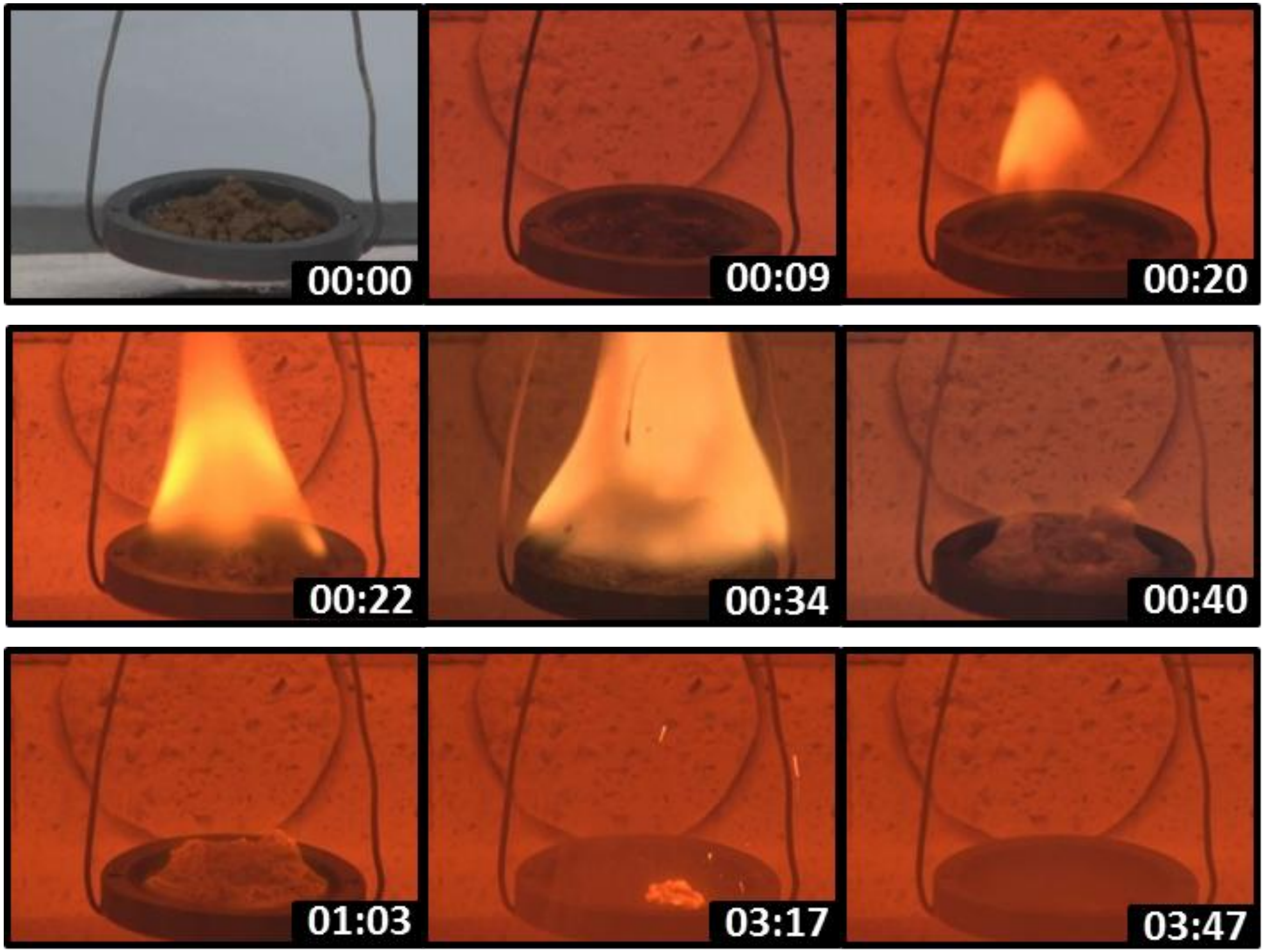
Hardwood Lignin Combustion

- Lignin A3 from aspen



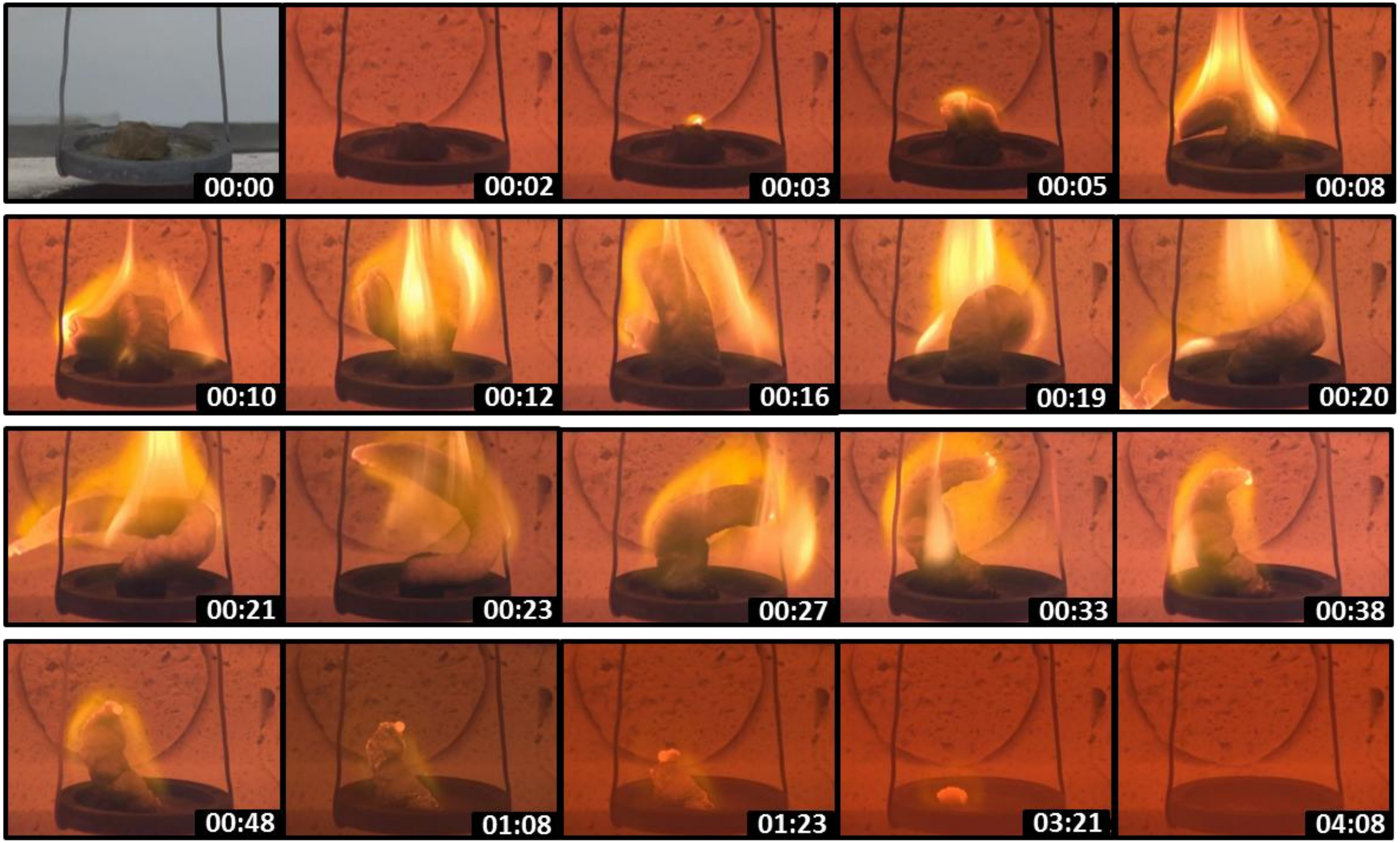
Hardwood Lignin Combustion

- Lignin B from eucalyptus

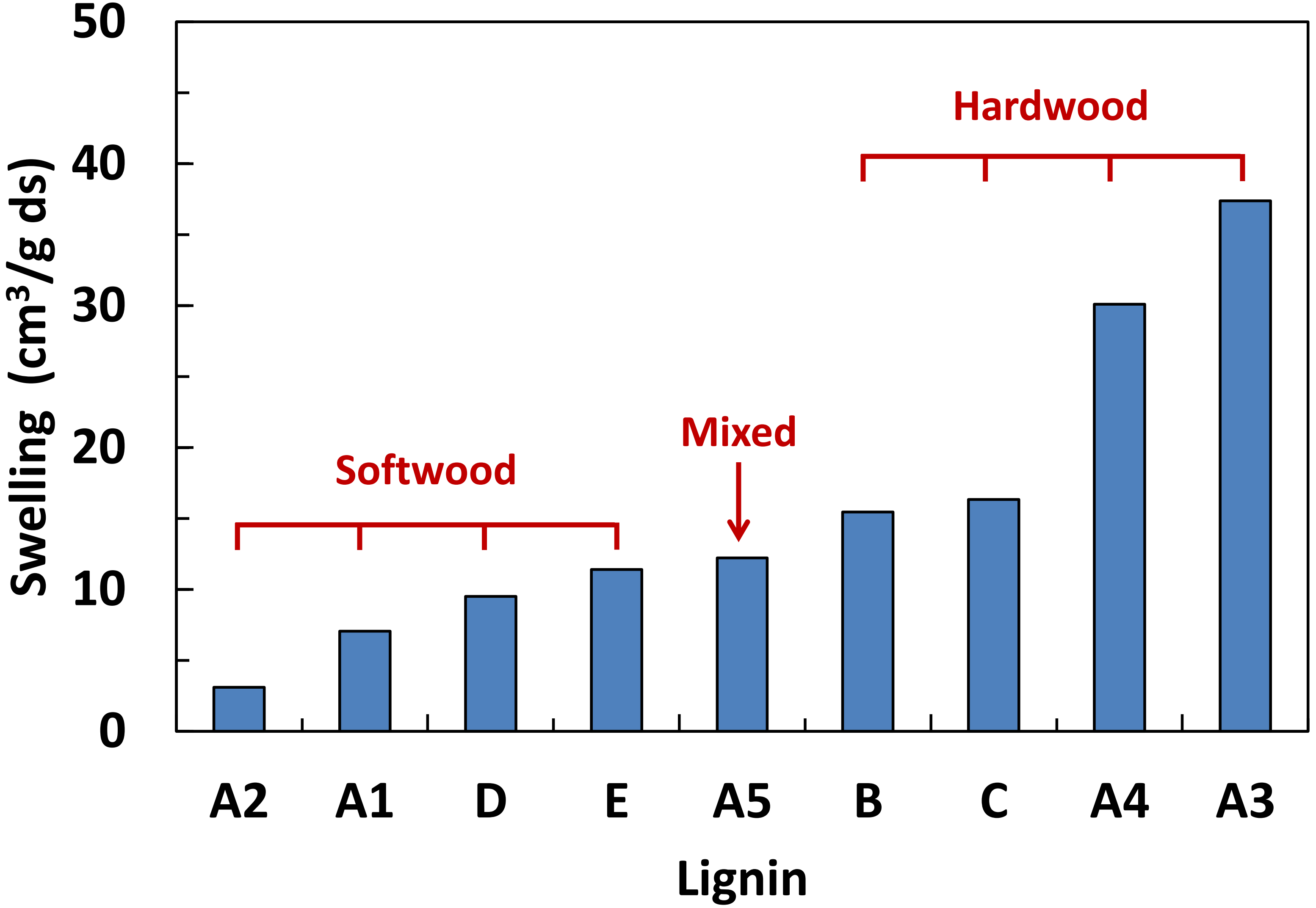


Hardwood Lignin Combustion

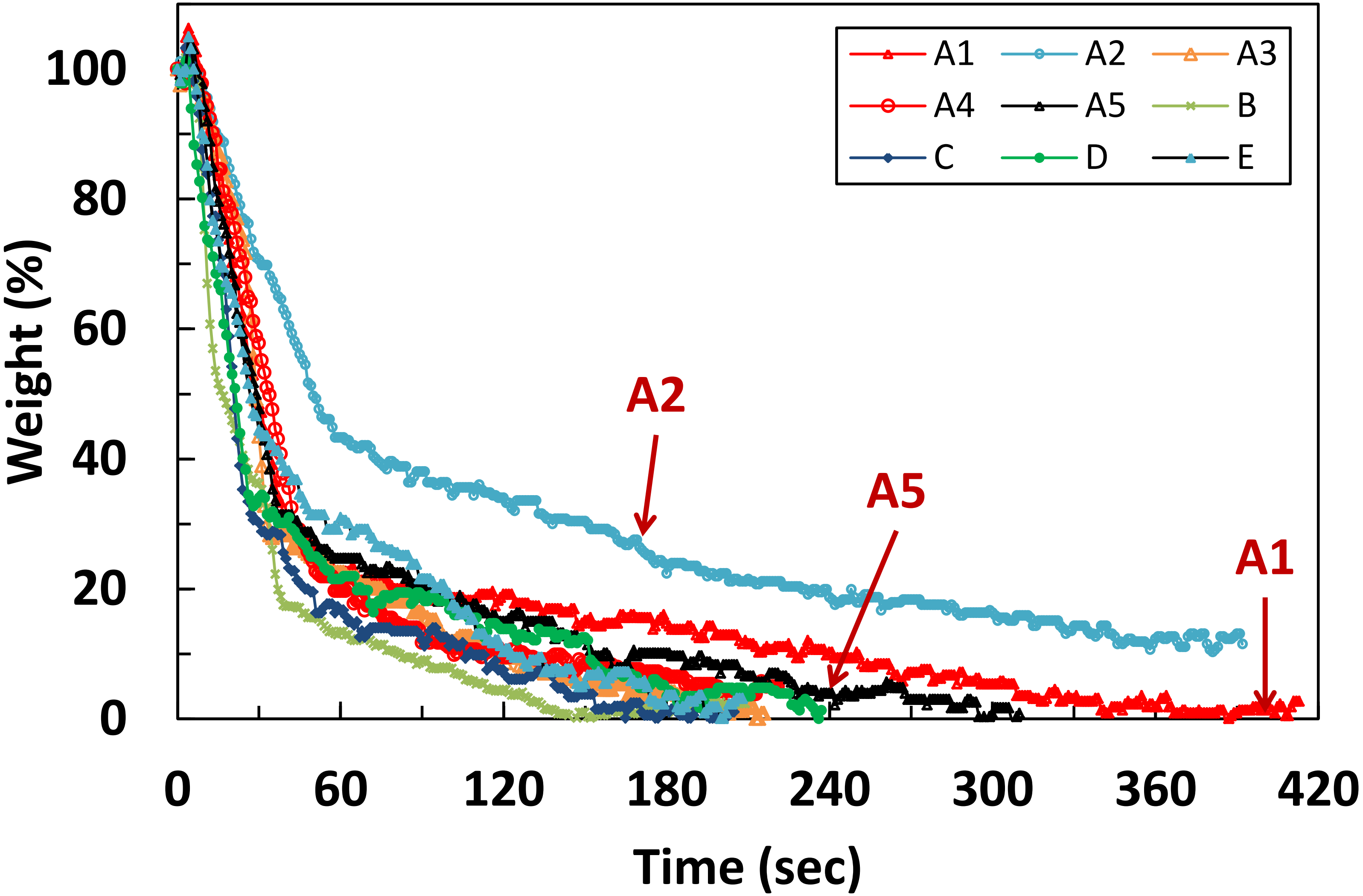
- Lignin A4 from aspen



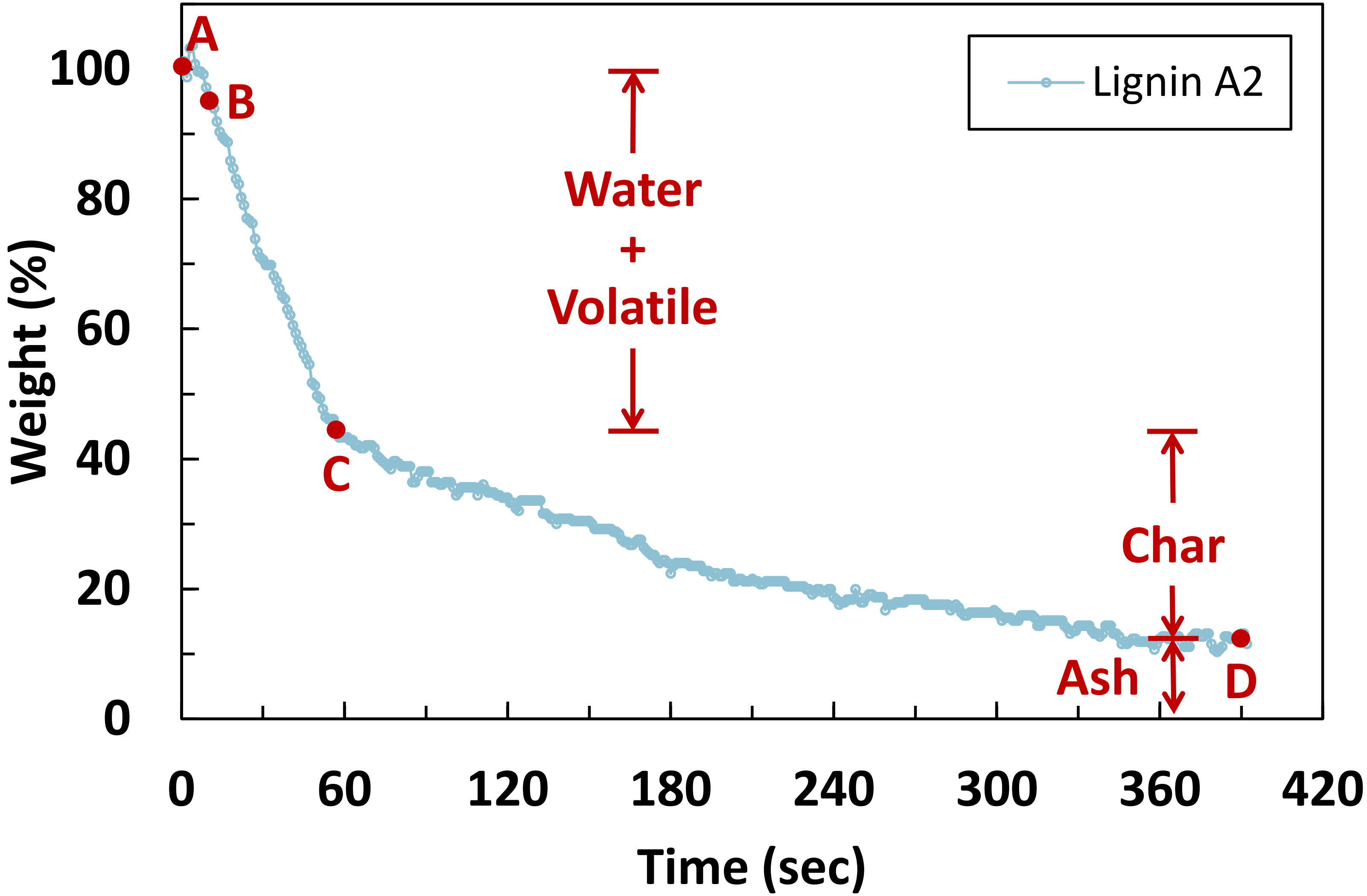
Lignin Swelling



Weight Change Profiles of 9 Lignin Samples



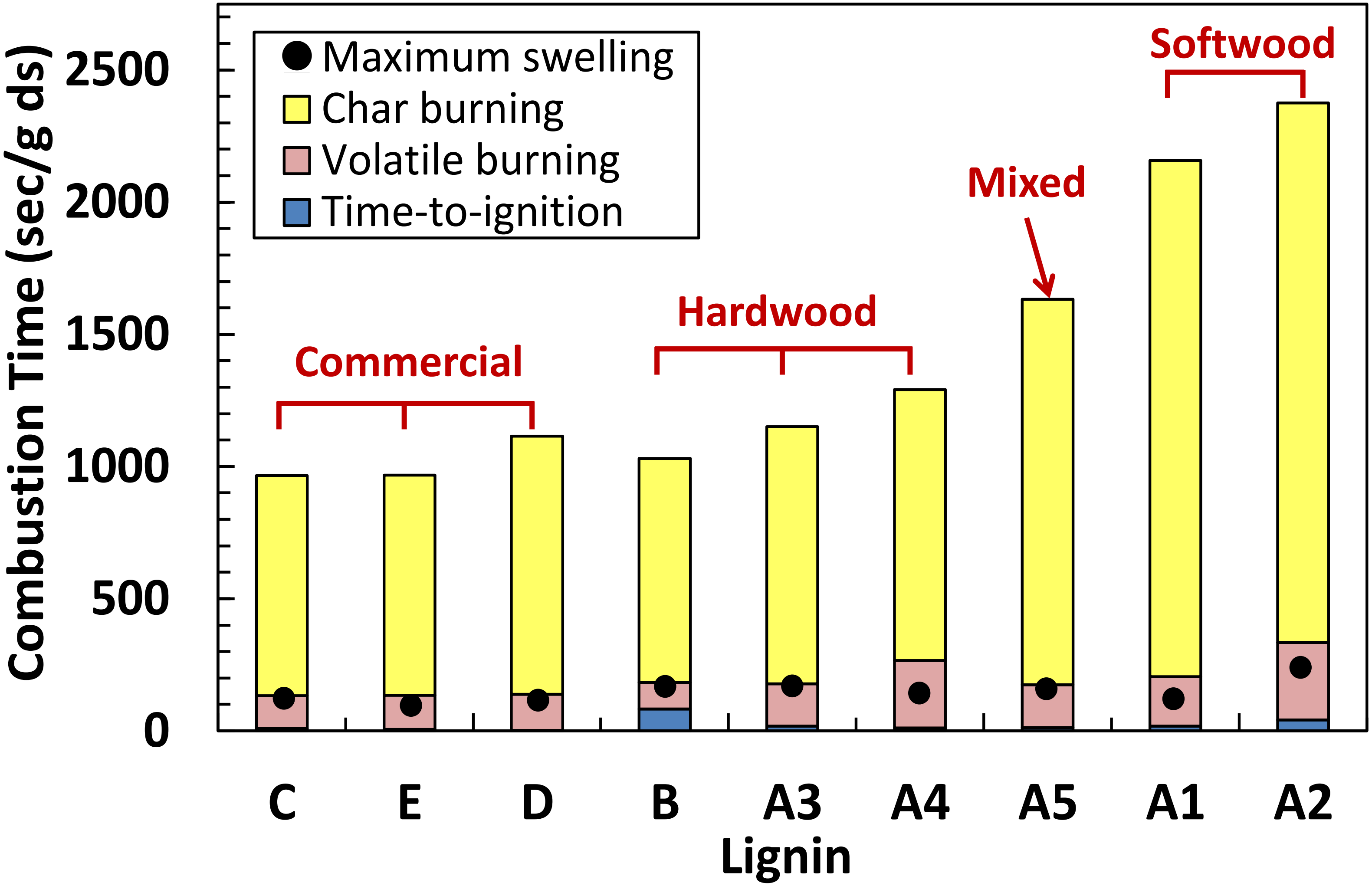
Combustion Stages



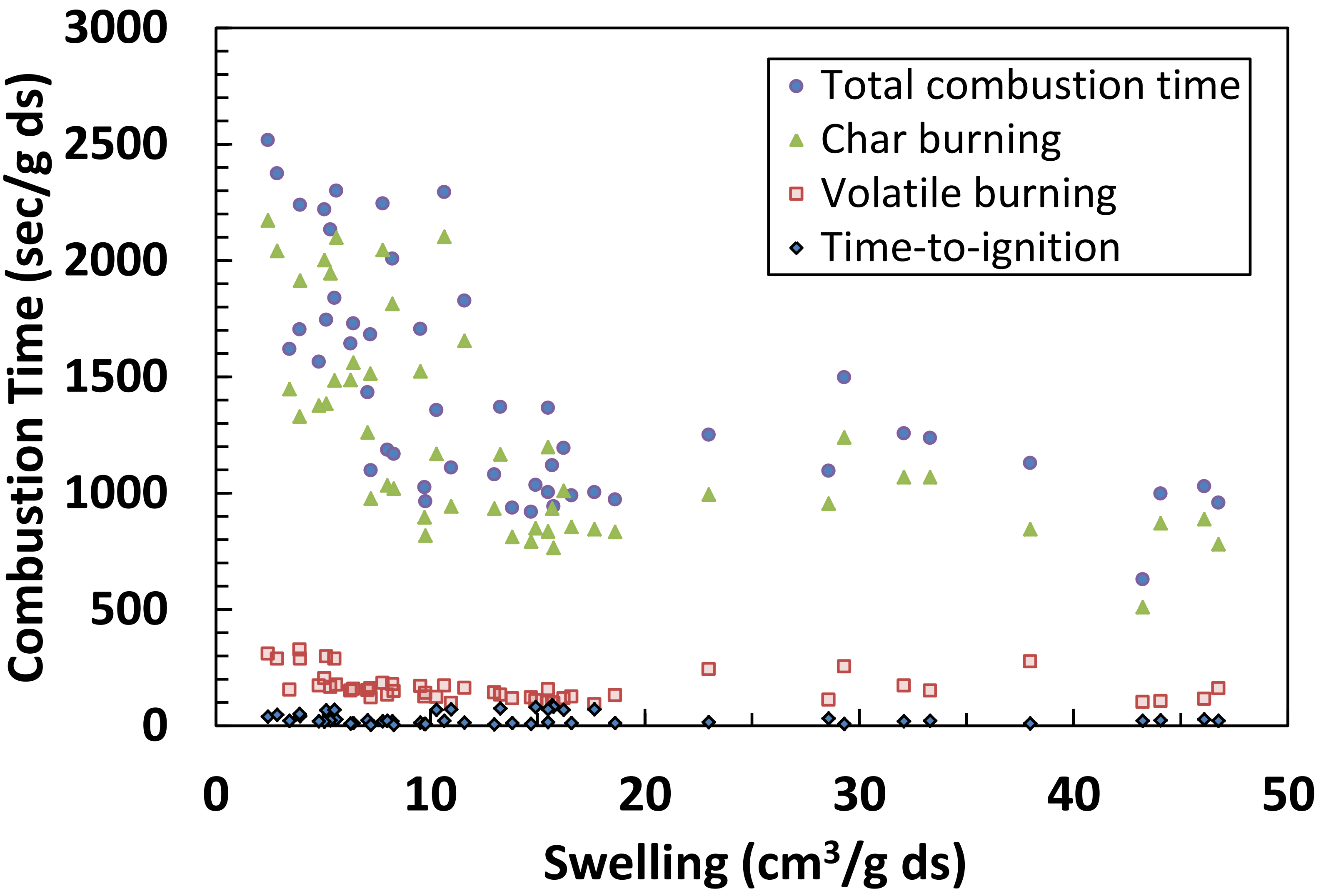
Lignin Compositions

Lignin	Wood Type	Wood Species	Water (wt%)	Volatile (wt%)	Char (wt%)	Ash (wt%)
A1	Softwood	Jack pine/spruce	7.1	61.8	28.9	2.2
A2	Softwood	Jack pine/spruce	19.0	34.8	34.5	11.7
A3	Hardwood	Aspen	9.9	60.2	29.1	0.8
A4	Hardwood	Aspen	18.8	54.7	17.7	8.8
A5	Mixed	Jack pine, spruce/aspen	4.8	61.5	31.9	1.8
B	Hardwood	Eucalyptus	56.9	24.3	16.4	2.4
C	Hardwood	Commercial	0	69.4	30.6	0
D	Softwood	Commercial	0	67.2	31.5	1.3
E	Softwood	Commercial	0	52.9	46.2	0.9

Combustion Stage Times



Combustion Time vs. Swelling



Summary

- Adding lignin-lean black liquor to its original black liquor decreased the heating value and the swelling of the mixed liquor
- The effect on swelling was insignificant for mixed liquors that contained less than 20% lignin-lean black liquor on a dry basis
- This implies that for a given mill, up to 20% of black liquor could be treated to extract lignin without altering the burning behaviour of black liquor

Summary

- **As with black liquor, the combustion behaviour of lignin was found to occur through 3 main stages:**
  - **Drying**
  - **Volatile burning**
  - **Char burning**
- **During the volatile burning stage**
  - **Hardwood (HW) lignin swelled significantly**
  - **Softwood (SW) lignin did not swell much**
  - **Mixed HW/SW lignin was somewhere in between**

Summary

- **Lignin that swelled more burned more quickly than lignin that swelled less**
- **Although the char content in lignin was about half of the volatile content, it took 10 times longer for the char to burn compared to the volatiles**

Acknowledgements

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