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PYROLYSIS OF BLACK LIQUOR IN A HIGH-INTENSITY ACOUSTIC FIELD

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ABSTRACT

This study presents the effects of acoustics on the primary yields of pyrolytic reactions of black liquor (a spent liquid from pulping processes in pulp and paper manufacturing) solid particles in an entrained flow reactor at gas temperatures between 400-700°C with flow rates of 5–20 SLPM. The particle sizes were around 125 μm. The acoustic intensities were 151 dB and frequencies were from 300–1000 Hz. At a gas temperature of 550°C, char yield was reduced by 10% and CO and CO_2 gas yields were increased by about 50-400% and 50-800%, respectively, with acoustics under various particle reaction (residence) times. The results of char and gas yields also show that the acoustic effects were more enhanced at the initial particle heat-up period. The fact that acoustics selectively enhanced the two endothermic reactions, organic carbon reduction, and inorganic (carbonate) carbon formation indicates that acoustics increased the heat transfer from the surrounding gas to the particles. SEM analysis of the char surfaces revealed that particles swelled much more and large bubbles were formed at the particle surface when particles were pyrolyzed with acoustic fields, further verifying the enhanced heat and mass transfer between the particle surfaces and the surrounding gas. At a gas temperature of 400°C, char, CO, and CO_2 yields were unchanged with acoustics due to a temperature too low for progression of tar secondary reactions. At a gas

temperature of 700°C, CO_2 yield increased by 30-80% with an acoustic field; whereas, CO and char yields were about the same, indicating that a critical heat and/or mass transfer rate has been achieved with or without acoustics and that secondary cracking of reactive tar functional groups forming CO_2 is more likely than is polymerization into char.

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INTRODUCTION

The behavior and yield of the pyrolytic products of coal, biomass, and other solid fuels dictate the energy requirements and processing conditions for gasifying the char carbon (Brink and Thomas, 1975). Char carbon gasification reactions require more energy input and proceed more slowly than do pyrolysis reactions. Hence, gasification would be more energy efficient if more of the carbon in these fuels was converted to combustible gases instead of char during pyrolysis. Therefore the study of the pyrolytic reactions has significant scientific and practical importance.

Black liquor, an aqueous solution containing dissolved organic and inorganic solids, is a by-product of the pulping process in pulp and paper manufacturing. The dissolved organic material is a complex substance derived from cellulose, hemicelluloses, lignin, and extractives in the wood. Combustion of black liquor has been a common practice in the pulp and paper industry, recovering 95% of the pulping chemicals, and supplying 45% of the energy requirement in pulp and paper manufacturing. Black liquor gasification has attracted great attention in recent years to obtain high-energy efficiency and operation safety in pulp and paper manufacturing. It has been found that gasification reactions of black liquor char produced from pyrolysis proceed very rapidly at gas temperatures as high as >900°C (Stigsson and Hesseborn, 1995). However, corrosion is severe at temperatures above the smelt, or inorganic burning residual of black liquor, melting point of about 700-800°C, which makes low-temperature black liquor gasification attractive. Unfortunately the product gas yield of black liquor pyrolytic reactions at temperatures below the melting point of the smelt is relatively low.

Numerous studies have shown that high-intensity acoustic fields can increase convective mass, momentum, and heat transfer between gas and solid or liquid phases, resulting in more efficient evaporation and combustion. Some examples are combustion of coal (Gupta and Rajan, 1991;

Lyman and Sabnis, 1982; Severyanin, 1969, and Carvalho et al., 1987) and gasoline and diesel fuel droplets (Blasczyk, 1991, Gemmen et al., 1990); sublimation of naphthalene spheres (Hodgins et al., 1957); and evaporation of water sprays (Rawson, 1988) and water and methanol droplets (Sujith, 1994). Acoustically enhanced heat and mass transfer can be attributed to three factors: (1) increased turbulent slip velocity between the particle and the gas phase due to oscillating gas sweeping past the particle (Lighthill, 1978 and Gemmen et al., 1990), for example, Gemmen et al. (1990) predicted that droplet evaporation can be increased by 160% due to acoustics-induced high droplet slip velocity; (2) increased particle reaction (residence) time due to particle levitation (Doinikov, 1996) when the acoustic radiation pressure overcomes the gravitational force on the particle; and (3) increased particle internal mass transfer due to the acoustic pressure pulsation at a pressure anti-node (Bartolome et al., 1969; Borisov and Gynkina, 1962). In the present research, we study the feasibility of applying acoustics to improve the primary product gas yield of pyrolytic reactions of black liquor (dried) at temperatures below the melting point of the smelt (< 700°C) in an entrained flow reactor. The objective of the study is to obtain fundamental understanding of the effects of acoustics on the primary yields of pyrolytic reactions of black liquor in idealized reaction conditions. Based on previous laboratory single black liquor drop combustion research (Grace and Frederick, 1998), the gasification of black liquor char proceeds much more slowly than the pyrolysis reactions under the temperature range of 400-700°C at atmospheric pressure. Therefore, the products obtained can be regarded from pyrolysis reactions and the gasification effect can be ignored in this study.

EXPERIMENTAL

Black Liquor Particles

Soda black liquor at 45% solids was obtained from a pulp mill (Mead Corp., Kingsport, TN). The liquor was mixed using a propeller-type paint mixer for 20 minutes. Five 200 mL samples were withdrawn, poured into a 35-cm-wide by 40-cm-long 304 stainless steel pan, and dried at 105°C in an oven with fresh air recirculation for about 6 days. The liquor was stirred twice each day during the drying process. The dried liquor was transferred to a ceramic jar of a ball mill that was filled with ceramic balls of 2.5 cm in diameter to grind. To obtain the particles with sizes around 125 μm that is favorable to achieve great slip velocity between the particle and the gas phase for acoustic enhancement (Rudinger, 1980), the particles were sifted through 106- and 125-μm mesh opening size. The composition of the dry black liquor solids was analyzed by certified laboratories and is listed in Table I.

Experimental Apparatus

An entrained flow reactor (EFR) was used to investigate the inflight pyrolysis of black liquor solid particles in a high-intensity resonant axial acoustic field, as shown schematically in Fig. 1. The reactor is about 1-meter long, which gives one complete pressure oscillation cycle at acoustic frequency of about 300 Hz. The reactor consists of the following sections: (1) reactor tube and support frame, (2) acoustic compression driver and air purge, (3) horizontal trombone tube, (4) N_2 gas preheater and 45° elbow, (5) particle feeder and 90° elbow, (6) vertical heated pyrolysis tube, (7) acoustic decoupler/char collector, (8) gas analyzer and product gas analysis system, (9) particle and gas flow visualization system, and (10) data acquisition system. The reactor wall was heated by ceramic heaters. The wall temperatures were maintained at 400, 550, or 700°C during the

experiments. Thermocouple measurements of the gas temperature indicated that gas temperature variation across the radial direction is very small (less than 20°C) at all experimental conditions. The gas temperature profiles measured along the reactor longitudinal direction with and without acoustics are very similar. Particles were pyrolyzed inflight in a steady gas flow with or without superimposed, acoustically induced gas oscillations. Particles were first entrained in the primary gas, and then injected into the pyrolysis reactor along the centerline of the downward flowing secondary gas. Particle reaction (residence) time was varied by externally heating different sections of the pyrolysis tube and by varying preheated gas velocity. Residue char particles eventually fell out of the pyrolysis tube and formed a pile on the bottom of the acoustic decoupler. The decoupler temperature was always less than 200°C within about 1.5 cm after the entrance from the reactor tube. This region of the decoupler was quenched with room temperature nitrogen. Condensed tar and fume settled out on a filter located at the exit of the decoupler. Char, tar, and fume were removed from the decoupler after completion of each experiment. Pyrolysis product gas passing through the filter was continuously analyzed for CO and CO_2 by an infrared absorption gas analyzer. Detailed design and operating procedures of the apparatus can be found in the work of Koepke (1998).

Analysis of Pyrolysis Products

Char yield, represented by the weight-percent (Wt%) of black liquor solids (BLS) converted to char, and the char total carbon yields, represented by the weight-percent (Wt%) of carbon in BLS converted to total (both organic and inorganic) carbon in char, were used to determine the extent of BLS particle pyrolysis reactions. The 95% confidence level of the char yield, which was based on three sets of triplicate experiments, spanned ±2.75 weight percentage points about the mean. For selected chars, total carbon and carbonate carbon in the char were measured by Huffman Laboratories

(Golden, CO). Organic carbon was calculated from the difference of total carbon and carbonate carbon. Total carbon in all the chars were measured in triplicates or quadruplicates.

A sufficient sensitive online hydrocarbon gas analyzer was not available in this study. However, off-line gas analysis of a pyrolysis product gas sampled midway through experimental runs using a gas chromatograph (GC) indicated very little hydrocarbon gases, such as CH_4, were produced compared to the amount of CO and CO_2 measured. Our off-line GC analysis agrees with the conclusion of Alen et al. (1994) that CH_4 yield is low in the 400-700°C gas temperature range. Therefore, a complete gas analysis was not conducted in this study and only CO and CO_2 were analyzed. CO and CO_2 yields were obtained through integration of the time-dependent concentrations of CO and CO_2 measured using the infrared instrument.

SEM imaging of char particle surfaces was performed to seek evidence of increased particle heatup rate and greater severity of pyrolysis with the application of an acoustic field, e.g., greater swelling, increased surface bubble formation, and particle porosity.

RESULTS AND DISCUSSION

The particle residence (reaction) time is used in this study to present the data. It was calculated using a one-D particle motion equation with the consideration of particle dispersion in radial direction. The acoustic force was assumed in the opposite direction of gravity and is sinusoidal. Cold flow visualization indicates that a 300-μm char particle levitates under an acoustic field of 970 Hz and 159 dB. Therefore the levitation force calculated using force balance under this acoustic condition represents the maximum amplitude of the acoustic force and is used in the particle motion equation to calculate particle residence time. Precise calculation of particle residence time is very difficult, in particular, under the acoustic conditions where the actual acoustics force is not

known. Several assumptions were made in our calculation: (1) particle mass loss is uniform through the reactor, (2) the drag coefficient of a black liquor particle (rough surface with rough layer of 10-15 μm obtained from SEM analysis) is about 80% of a smooth sphere based on the work of Fuchs (1964), (3) the average particle injection velocity is equal to the carrier gas velocity. Detailed analysis of particle residence time can be found in the dissertation by Koepke (1998).

Char Yield

We compared the char yields obtained from the pyrolysis of inflight particles with and without acoustic fields of 146-154 dB and 310-1000 Hz at gas temperatures of 400, 550, and 700°C to show the effects of acoustics on the pyrolytic reactions. The results indicate that at gas temperatures of 400 and 700°C, the differences between the char yields obtained with and without acoustics were not significant for similar particle reaction (residence) times as shown in the Fig 2. At a gas temperature of 550°C, char yields obtained with an acoustic field of 151 dB and 970-1000 Hz were about 6-7 wt% lower than those obtained without acoustics over the range of particle reaction times studied. This translates to about 10% more reduction in char. At the initial heat-up period, the char yield with acoustic field is about 9 wt% lower than that without acoustics. The data indicate that the acoustic effect on char yield is very significant at a temperature of 550°C. The results, as shown in Fig. 2, indicate that the enhancement of char reduction was due to either the enhanced heat and mass transfer at the particle surface or the increased particle internal mass transport due to strong pressure oscillation. It is not, however, due to the increased particle reaction (residence) time because even though acoustics do increase the particle residence time in the reactor, the comparisons are made under approximately the same mean particle reaction times. Furthermore, experiments conducted without acoustics but with a steel wool plug (infinitively long particle reaction time)

indicated that char yield was higher than those under similar experimental conditions with acoustics without steel wool plug (finite particle reaction time). However, due to the limited measurement techniques available and the difficulties in the experiments, in-situ particle temperature measurements were not conducted in this study to verify the enhanced heat transfer between the gas phase and the particles.

The fact that acoustic enhancement on char reduction was significant only at a gas temperature of 550°C indicates that perhaps a critical heating rate exists at which enhanced heat transfer can help char reduction. Below this heating rate, the reaction temperature is too low to be kinetically significant. Beyond this heating rate, significant char reduction has been achieved and further reduction is not possible due to kinetic limit. Because of the complex nature of the reactions involved in black liquor pyrolysis, complete kinetic analysis was not possible. We conducted a kinetic analysis using a two-parallel-competing-reaction model used by Kobayashi et al. (1976). The analysis indicates that the kinetic model predictions qualitatively agree with the measurements as shown in Fig. 3. However, the model predicted less difference in char yield between experiments with and without acoustics at gas temperature of 550°C. Furthermore, the model predicted a constant char yield value for mean particle residence time longer than one second. Failure of the model indicates that a two-parallel-competing-reaction model is insufficient and that pyrolysis reactions must also be occurring in series. The model also predicted that a gas temperature of 400°C is too low to promote complete pyrolysis (not shown). At a gas temperature of 700°C, pyrolysis is completed very rapidly at the particle heat-up rates obtainable with or without acoustics. At a gas temperature of 550°C, most pyrolysis reactions have been completed, however, gas releasing reactions are still slow and an increased particle heat-up rate could result in a higher rate of gas production.

As show in Fig. 2, a sound pressure level of greater than 146 dB is required to cause a significant reduction in char yield. Reducing the frequency from 970 to 310 Hz caused char yields to increase by about 2 wt%. This is because the heat and mass transfer enhancement due to increased turbulent slip velocity depends on the frequency response of the particles to the pressure oscillation (Rudinger, 1980). From a flow visualization study (Koepke, 1998), we found that at a frequency of 970 Hz, particle flow was much more out of phase (great slip velocity) with the gas flow as indicated by the three zones of particle levitation within the reactor at the pressure nodes, which agrees with the study of Doinikov (1996).

Char Chemical Composition

Char chemical composition in terms of organic and inorganic carbon directly relates to chemical recovery efficiency and fuming (carbonate aerosols) formation in pyrolysis. We analyzed the dry black liquor solids and eight chars that were obtained from inflight particle pyrolysis experiments with and without an acoustic field of 151 dB and 950-1000 Hz for total carbon and carbonate carbon. The results indicate that at the gas temperature of 550°C, the wt% of BLS C, or percent of the carbon in BLS, as total and organic carbon in the char obtained with acoustics were correspondingly lower than those obtained without acoustics, as shown in Figs. 4-5. The wt% of BLS C as total carbon was on average about 3.5 wt% lower, or reduced by about 15%. It was more than 6 wt% lower at the initial heat-up period, or a reduction of about 25%. Similar behaviors were observed for the wt% of BLS C as organic carbon, as shown in Fig. 5. However, we found that the wt% of BLS as inorganic (carbonate) carbon in the char obtained with acoustics were correspondingly higher than those obtained without acoustics, as shown in Fig. 6. Therefore, acoustics selectively enhanced the organic carbon reduction and carbonate carbon formation. The

fact that both reactions are endothermic indicates that perhaps it is the acoustically enhanced heat transfer that causes this selectivity of char composition.

The results in Figs. 4-6 also show that the differences of the wt% of BLS C, or the percentage of the carbon in BLS, as total and organic carbon in the char were greatest between experiments with and without acoustics for the shortest (0.18 m) pyrolysis tube heated length, or mean particle residence time (between 0.23 and 0.26 s). This reveals that acoustic enhancement is more significant at the initial particle heat-up period.

CO and CO_2 Yields

Figs. 7 and 8 show CO and CO_2 yields obtained with and without acoustics under conditions of 0.18, 0.48, and 0.81 m pyrolysis tube heated lengths, 0.21-3.88 s mean particle residence times, 0.32-6.59 s secondary gas space-times, and a gas temperature of 550°C. CO yields obtained with acoustics were always correspondingly higher than those obtained without acoustics, indicating the acoustic enhancement in combustible product gas yield. CO_2 yields with an acoustic field of 151 dB were also at least 1.5 wt% higher than those obtained without acoustics for the same particle reaction times. On average CO and CO_2 yields were increased by about 50%. The CO and CO_2 yields obtained using the 0.18 m pyrolysis tube heated length were increased by about 400 and 800%, respectively, with acoustics. Greater production rates and yields of CO and CO_2 obtained in the 0.18-m pyrolysis tube heated length using acoustics indicate that pyrolysis was more severe during the particle heat-up period. This argument was also drawn from the char reduction data as discussed in the previous section. The fact that acoustics most significantly increased CO_2 yield and reduced char yield at 550°C, at which reactive tars may undergo secondary cracking to form CO_2 or polymerize into char unless the tar can escape, indicates that acoustics enhanced the transport of reactive tar species away from the pyrolyzing particle.

Figs. 7 and 8 also show that CO_2 yield increased by 30-80% with an acoustic field, whereas CO and char yields were about the same at a gas temperature of 700°C, which indicates that a critical heating and/or mass transfer rate has been achieved with or without acoustics. Therefore, further reduction of char and formation of CO is not possible. The increased CO_2 yield can be attributed to the secondary cracking reactions of tar functional groups to form CO_2 and the suppressed tar polymerization reactions onto char.

Our experiments also indicate that CO and CO_2 yields were unchanged with an acoustic field at a gas temperature of 400°C due to a temperature too low for the progression of tar secondary reactions.

Product Mass Balance

We conducted a mass balance analysis from the measured yields of the pyrolytic products at a temperature of 550°C to demonstrate that the reported char yield decreases are consistent with the reported increases in CO and CO_2 due to acoustic enhancement. Table II lists the weight % of char, CO, and CO_2 yields as total black liquor solids mass at the three tested heated tube length of 0.18, 0.48, and 0.81 meters. The acoustics data were from experiments with acoustic intensity of 151 dB and frequencies were between 950 and 970 Hz. We also listed the unaccounted mass that is mainly due to tar release. Tarry liquid was coated on filters and was observed in experiments. The unaccounted tar yield is about 15% by difference. The results clearly show that acoustics reduced char yield by about 10% and increased tar yield by about 20% on average, in addition to the increases in CO and CO_2 yields of 50-400% and 50-800%, respectively, that were reported early.

SEM Analysis of the Particle Surface

To verify that the acoustics enhanced heat and mass transfer between the particles and the surrounding gas, we conducted SEM analysis of the surfaces of char particles to seek physical evidence. The discussion in this section are based on the SEM images obtained at the reactor temperature of 550°C. It is known from a single black liquor drop combustion study (Adam and Frederick, 1988) that a black liquor drop swells more and releases more volatiles with increased heat and mass transfer from the surrounding gas. The SEM measurements indicate that with an acoustic field of 151 dB and 1000 Hz and 0.18 m pyrolysis tube heated length, char particles are slightly more swollen and contain many more cellular bubbles that are larger in diameter and tend to protrude from the particle surface, as shown in Fig. 9a, compared to those obtained without acoustics, as shown in Fig. 9b. As reactions continue, the bubbles should grow and become more porous due to volatile release. With acoustics, large cellular surface bubbles are present on the char particle surface and the particles are more porous, as shown in Fig. 10a. However, this type of surface morphology is not visible on the surfaces of char obtained without acoustics, as shown in Fig.10b, indicating that particle pyrolysis was not as severe, though the mean particle residence time of the experiment shown in Fig. 10b was longer than that in a similar experiment shown in Fig 10a, with acoustics. The SEM study clearly shows the effects of acoustic field on black liquor particle swelling characteristics due to enhanced heat and mass transfer between the particle surface and the surrounding gas.

SUMMARY

We studied the acoustic effects on the primary product yields of pyrolysis of black liquor dry particles in an entrained reactor. Significant reduction of char yield was observed with the application of an acoustic field of intensity 151 dB or higher at a gas temperature of 550°C. Increased yields of product gases CO and CO_2 were also observed with acoustics. The SEM analysis

of the surface morphology of char particles obtained from black liquor pyrolysis reactions showed that the particles were much more swollen and large cellular surface bubbles were present on the char particle surface under acoustic reaction conditions compared to those obtained without acoustics. The results from SEM analysis indicate that enhanced heat and mass transfer between the particles and the surrounding reaction gas contributed to the difference on product yields of the pyrolytic reactions of black liquor. The fact that acoustic enhancement on char reduction was significant only at a gas temperature of 550°C indicates that the reactions are kinetically controlled and the role that heat and mass transfer enhancement can play is limited to certain reaction conditions. The implication of the present study is that until char gasification rates can be significantly increased at a lower reaction temperature of approximately 550°C compared to those at >700°C, by catalytic or other means, there is no advantage to be gained by significantly increasing heat and/or mass transfer rates during pyrolysis/char gasification at gas temperatures ≤ 700°C.

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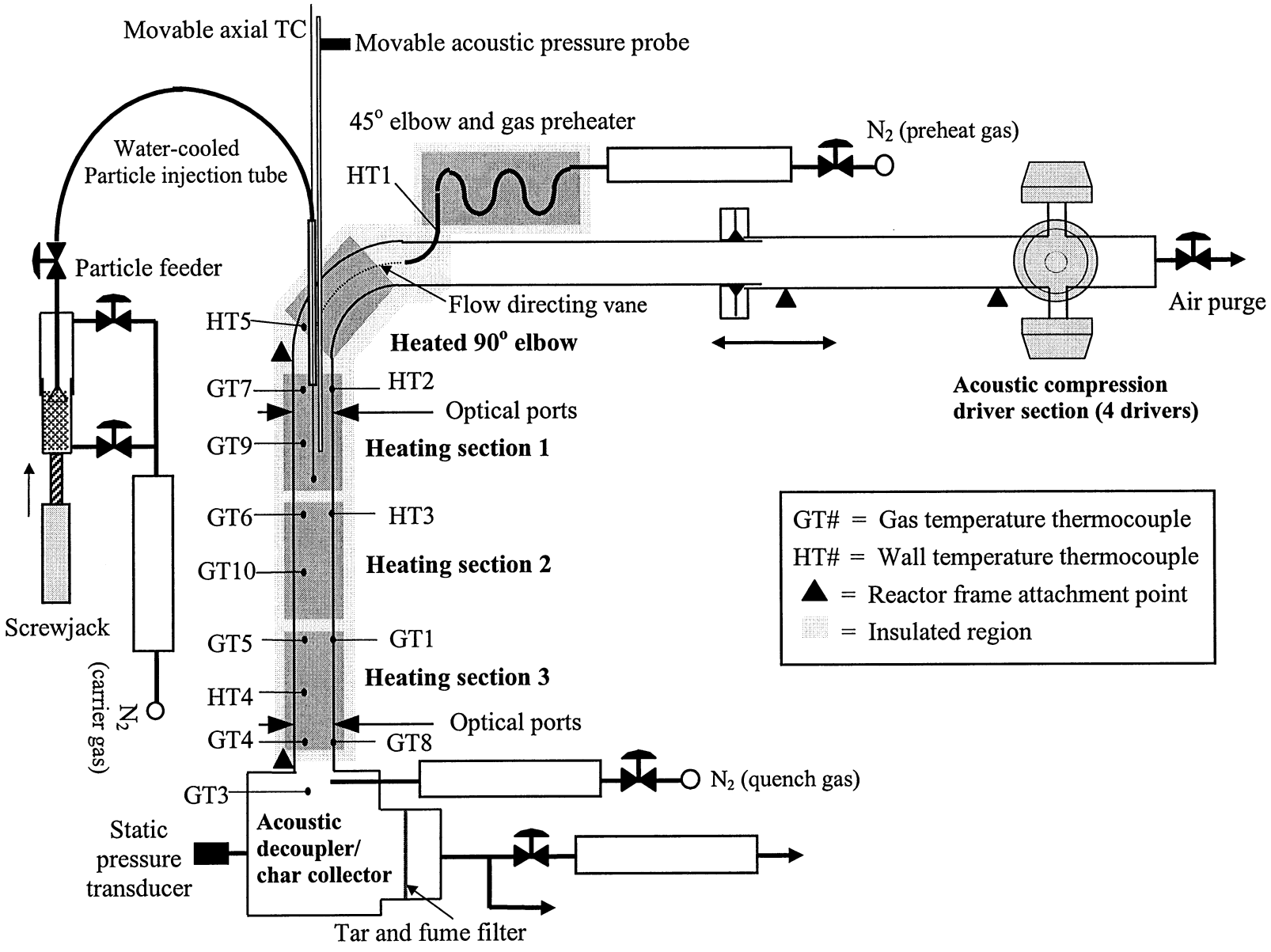
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Movable acoustic pressure probe
45° elbow and gas preheater
N2 (preheat gas)
Water-cooled
Particle injection tube
HT1
Particle feeder
Flow directing vane
Air purge
HT5
Heated 90° elbow
GT7
HT2
Optical ports
Acoustic compression
driver section (4 drivers)
GT9
Heating section 1
GT6
HT3
GT10
Heating section 2
GT# = Gas temperature thermocouple
HT# = Wall temperature thermocouple
= Reactor frame attachment point
= Insulated region
Screwjack
GT5
GT1
Heating section 3
HT4
N2
(carrier gas)
Optical ports
GT4
GT8
N2 (quench gas)
GT3
Static
pressure
transducer
Acoustic
decoupler/
char collector
Tar and fume filter

Fig. 1

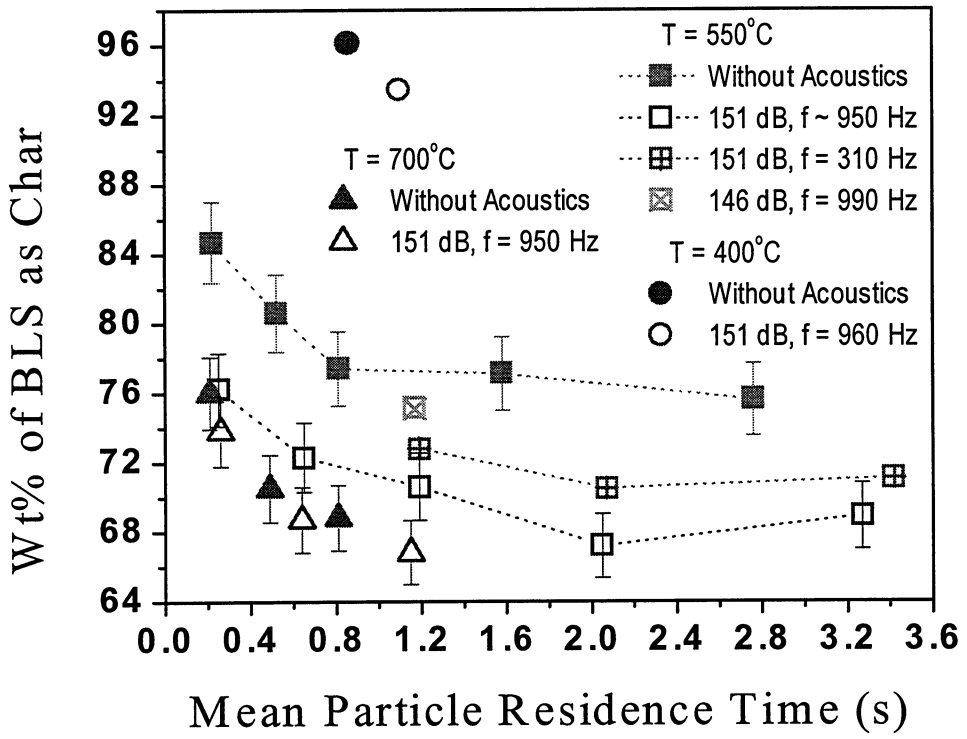

Wt% of BLS as Char
96
92
88
84
80
76
72
68
64
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
Mean Particle Residence Time (s)
T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
151 dB, f = 310 Hz
146 dB, f = 990 Hz
T = 700°C
Without Acoustics
151 dB, f = 950 Hz
T = 400°C
Without Acoustics
151 dB, f = 960 Hz

Fig. 2

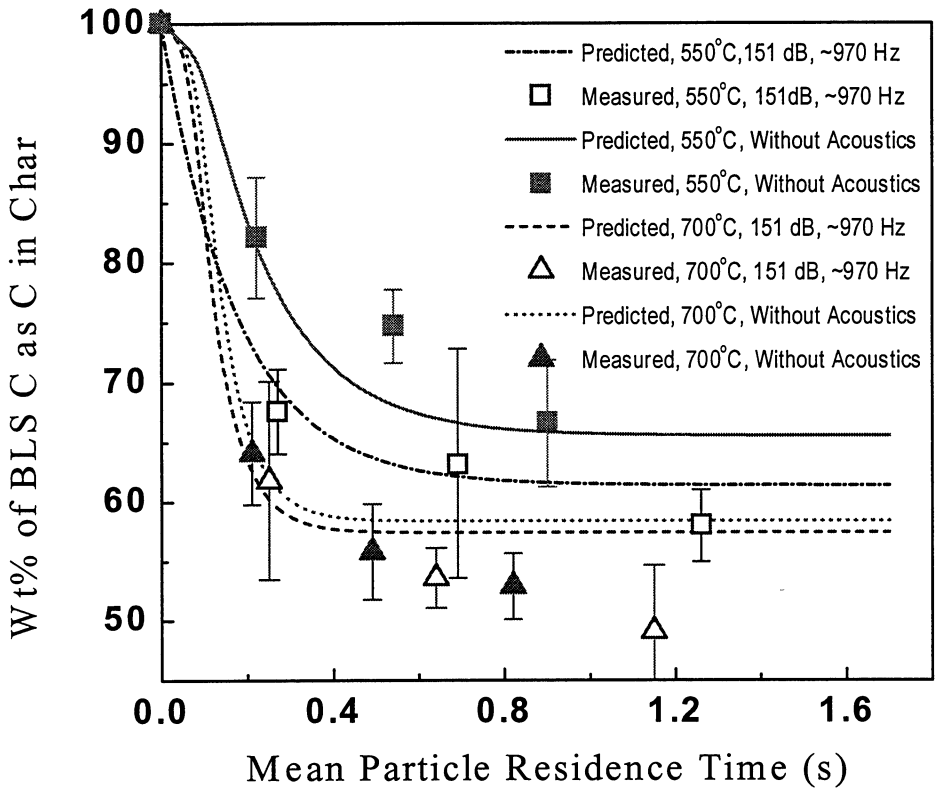

Predicted, 550°C,151 dB, ~970 Hz
Measured, 550°C, 151dB, ~970 Hz
Predicted, 550°C, Without Acoustics
Measured, 550°C, Without Acoustics
Predicted, 700°C, 151 dB, ~970 Hz
Measured, 700°C, 151 dB, ~970 Hz
Predicted, 700°C, Without Acoustics
Measured, 700°C, Without Acoustics
Wt% of BLS C as C in Char
100
90
80
70
60
50
0.0
0.4
0.8
1.2
1.6
Mean Particle Residence Time (s)

Fig. 3

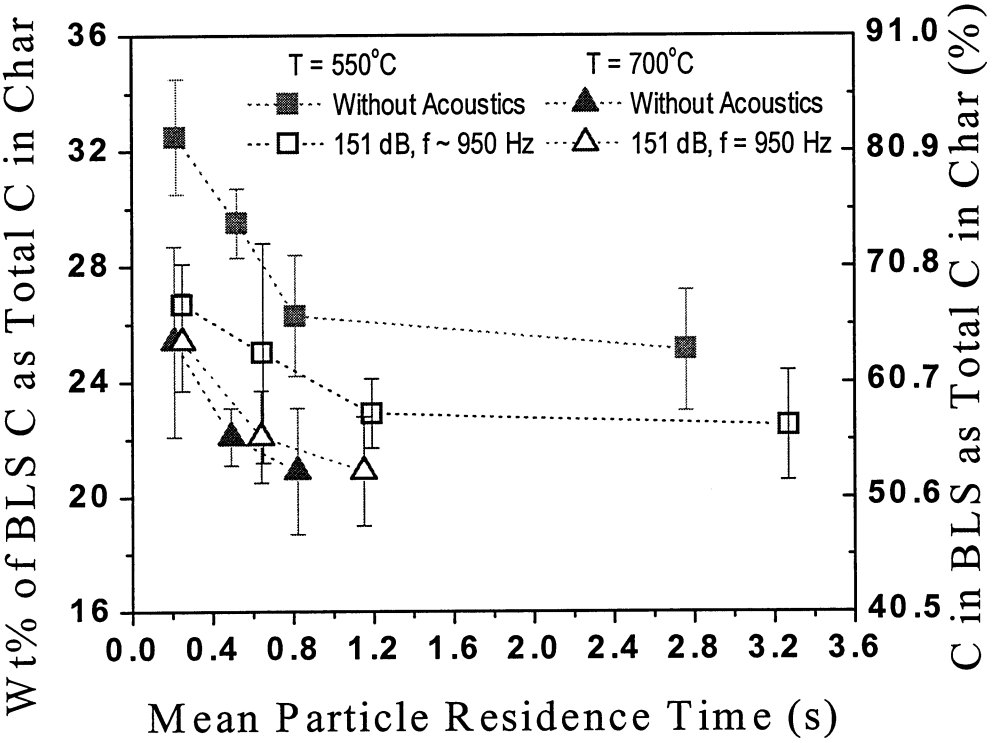

T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
T = 700°C
Without Acoustics
151 dB, f = 950 Hz
Wt% of BLS C as Total C in Char
C in BLS as Total C in Char (%)
Mean Particle Residence Time (s)
36
32
28
24
20
16
91.0
80.9
70.8
60.7
50.6
40.5
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6

Fig. 4

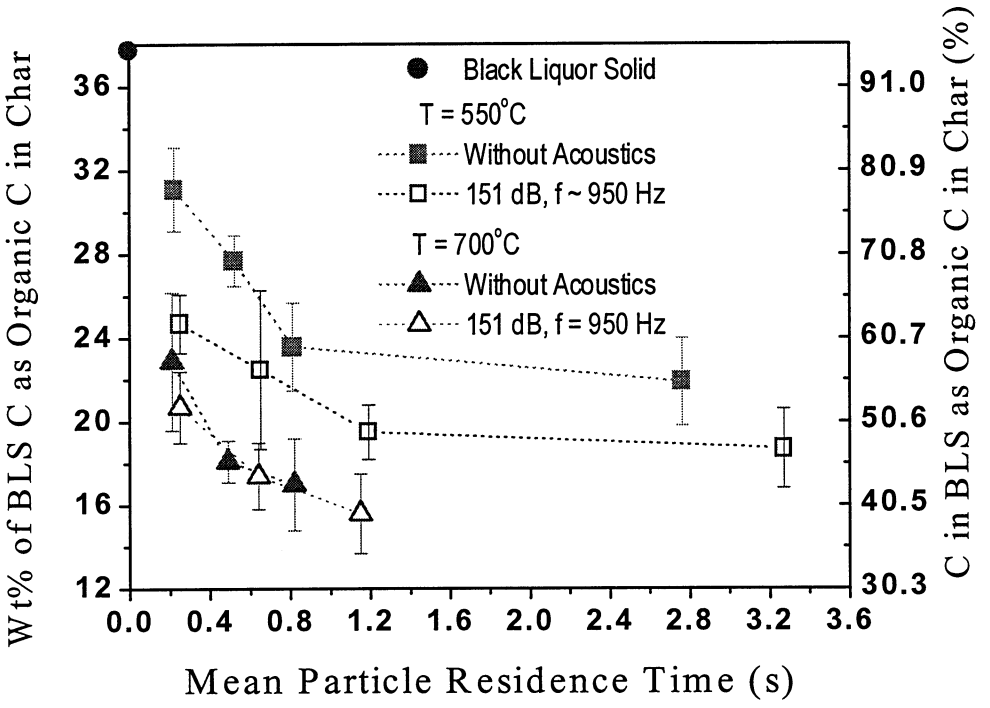

Black Liquor Solid
T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
T = 700°C
Without Acoustics
151 dB, f = 950 Hz
Wt% of BLS C as Organic C in Char
C in BLS as Organic C in Char (%)
Mean Particle Residence Time (s)
36
32
28
24
20
16
12
91.0
80.9
70.8
60.7
50.6
40.5
30.3
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6

Fig. 5

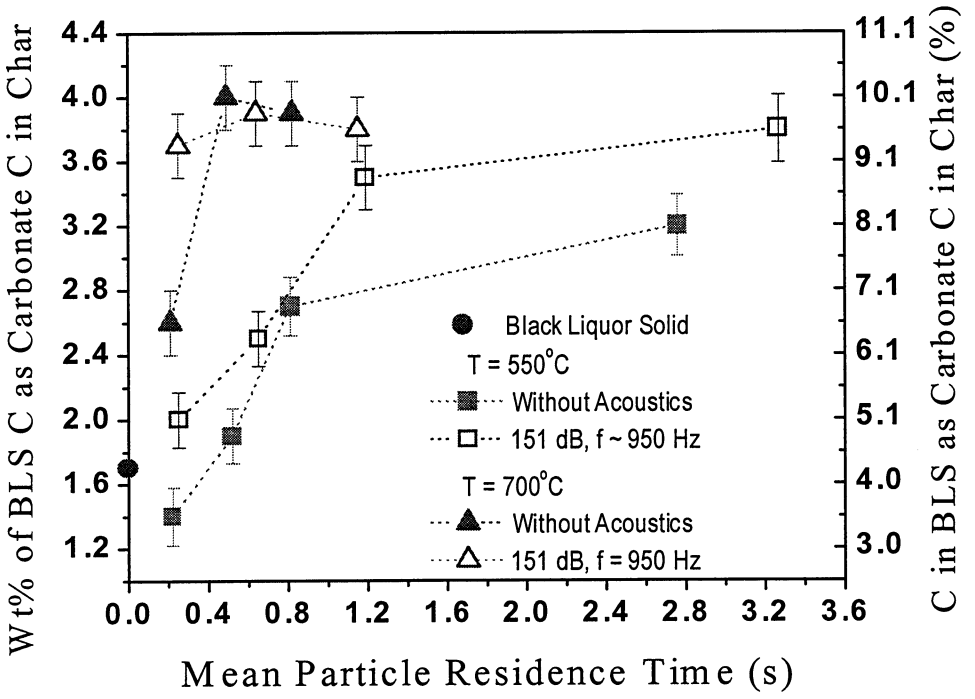

Wt% of BLS C as Carbonate C in Char
C in BLS as Carbonate C in Char (%)
Mean Particle Residence Time (s)
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
11.1
10.1
9.1
8.1
7.1
6.1
5.1
4.0
3.0
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
Black Liquor Solid
T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
T = 700°C
Without Acoustics
151 dB, f = 950 Hz

Fig. 6

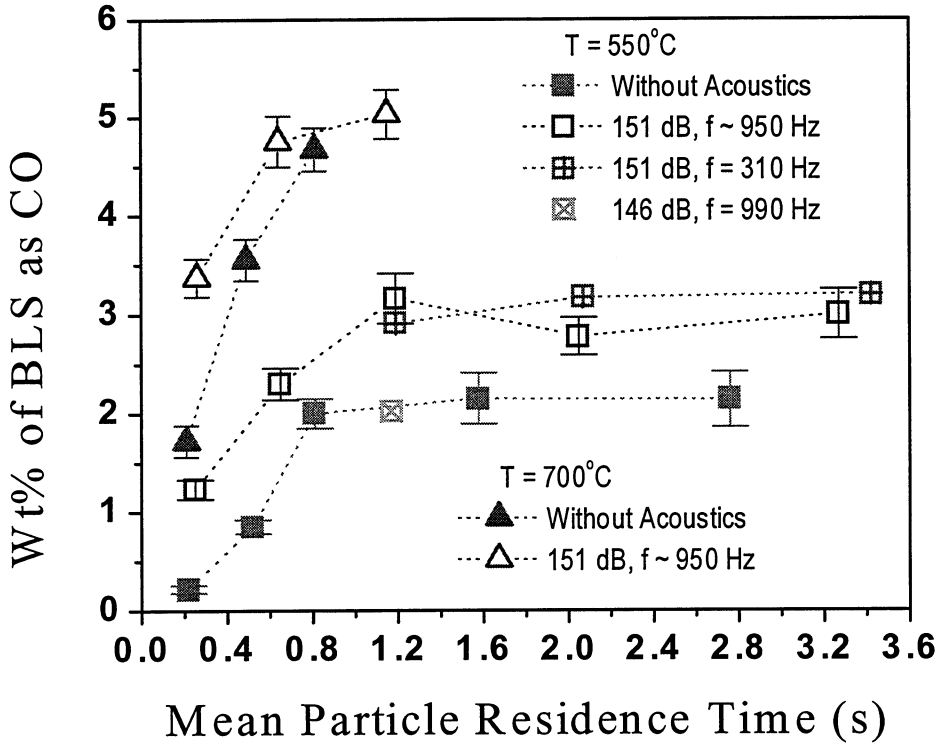

Wt% of BLS as CO
Mean Particle Residence Time (s)
T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
151 dB, f = 310 Hz
146 dB, f = 990 Hz
T = 700°C
Without Acoustics
151 dB, f ~ 950 Hz
0
1
2
3
4
5
6
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6

Fig. 7

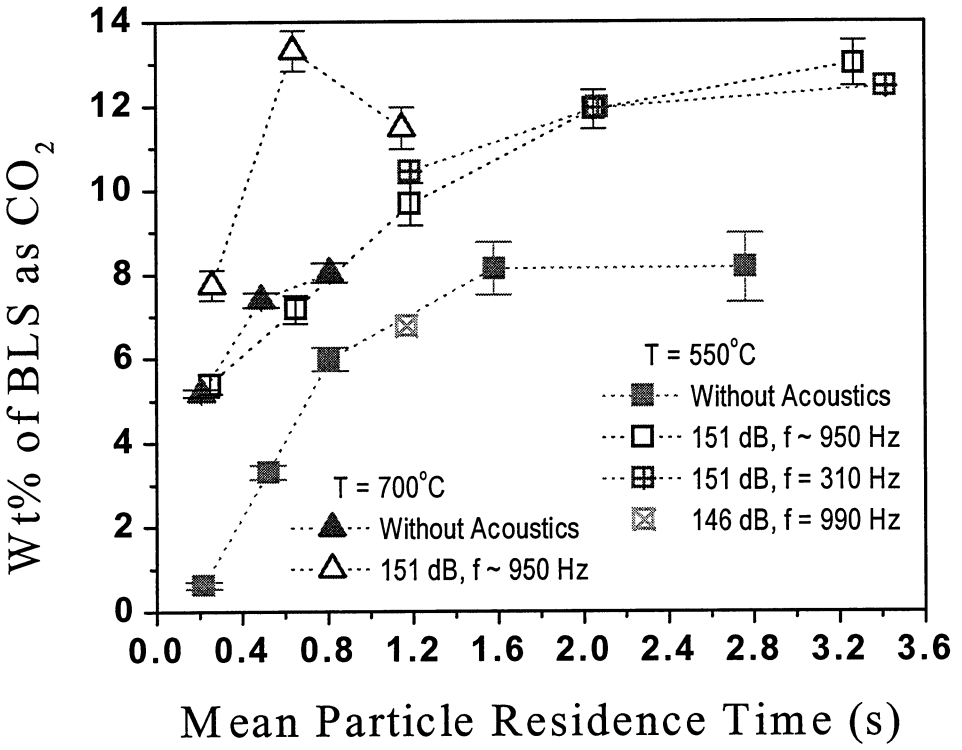
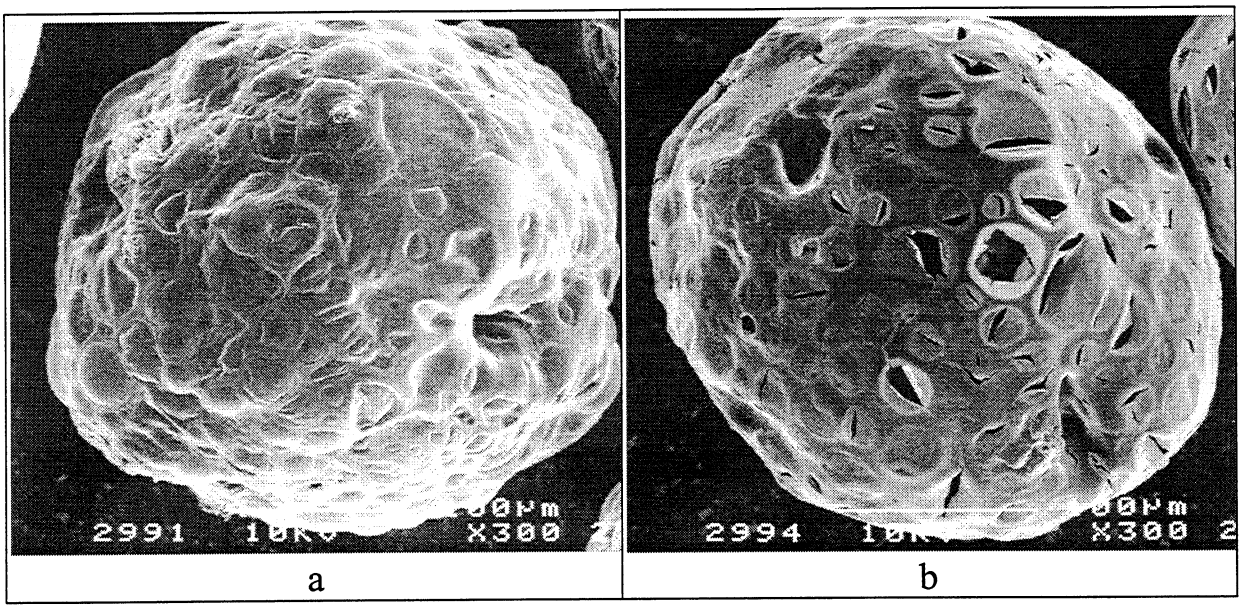
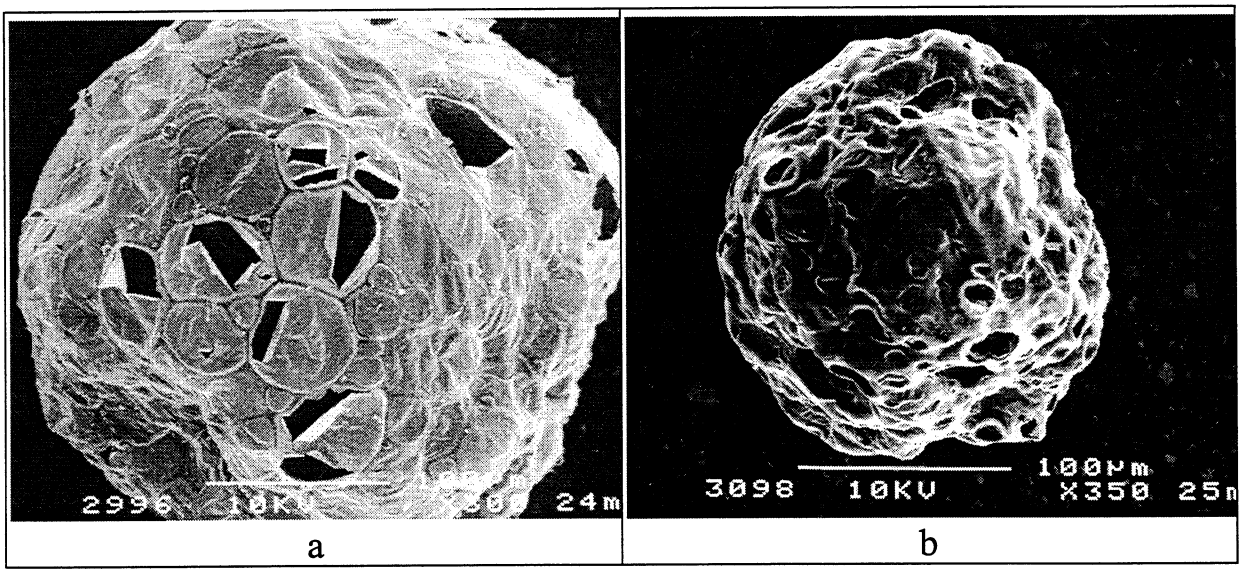

Wt% of BLS as CO_2
Mean Particle Residence Time (s)
0
2
4
6
8
10
12
14
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
T = 550°C
Without Acoustics
151 dB, f ~ 950 Hz
151 dB, f = 310 Hz
146 dB, f = 990 Hz
T = 700°C
Without Acoustics
151 dB, f ~ 950 Hz

Fig. 8



a b

Fig. 9. SEM image of a single char particle obtained at a gas temperature of 550°C with 0.18 m pyrolysis tube heated length and 0.38 s gas space time (gas flow rate). (a) with acoustics of 151 dB and 1000 Hz and 0.27 s particle residence time; (b) without acoustics and 0.23 s particle residence time.



a b

Fig. 10 SEM image of a single char particle obtained at a gas temperature of 550°C with 0.81 m pyrolysis tube heated length. (a) with acoustics of 151 dB and 990 Hz, 1.26 s particle residence time, and 1.72 gas space time; (b) without acoustics, 2.77 s particle residence time, and 6.59 gas space time.

Table I: The Composition of Black Liquor Solids

Element	**Wt% of Black Liquor Solids**
Carbon	39.37 (39.52[a])
Hydrogen	3.60
Oxygen[b]	34.45 (34.30)
Sodium	21.23
Sulfur	0
Potassium	0.90
Chlorine	0.45

a mean of total carbon measurements by Huffman Labs, Inc., Golden, CO, and one total carbon measurement by Galbraith Labs, Inc.

b by difference

Table II: Mass Balance Analysis of the Pyrolytic Products. Acoustics intensity was 151 dB and frequency was about 950-1000 Hz.

Heated Tube Length	Wt% of BLS as	Without Acoustics (%)	With Acoustics (%)	Difference (%)
0.18 m	Char	84.7	76.2	-8.5
	CO	0.3	1.2	0.9
	CO_2	0.6	5.4	4.8
	Unaccounted*	14.4	17.2	2.8
0.48 m	Char	80.6	72.3	-8.3
	CO	0.9	2.3	1.4
	CO_2	3.3	7.2	3.9
	Unaccounted*	15.2	18.2	3.0
0.81 m	Char	77.6	70.6	-7.0
	CO	2.0	3.2	1.2
	CO_2	6.0	9.7	3.7
	Unaccounted*	14.4	16.6	2.1

* Unaccounted is mainly due to tar release.