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Gasification of Black Liquor with the Addition of Secondary Sludge

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Abstract

The effects of secondary sludge addition on black liquor gasification were studied. Additions of 0, 5, 10, and 15% secondary sludge solids to hardwood black liquor solids were considered. Gasification temperatures were 700 and 900°C. Residence times were 0.2, 0.7, and 1.2 seconds. Gasification was performed in a laminar entrained flow reactor. Although both amount and rate of organic carbon conversion increased with temperature, the percentage of sludge addition did not affect percent of feed carbon recovered as organic carbon. Isobutyl and ethyl mercaptan, as well as carbon disulfide, were not produced in reportable quantities. Recoveries were expressed on a percentage-of-feed-element basis. Recovery of sulfur in char was higher for the 100/0 (black liquor/secondary sludge) feed than for the 85/15 feed. Recoveries of H_2S were higher for purer (less sludge added) feed stocks for all experiments except those performed 900°C/1.2 seconds residence time. Recoveries of methyl mercaptan, n-propyl mercaptan, carbon disulfide, and ammonia were relatively independent of sludge addition. Recoveries in char of magnesium, vanadium, and aluminum were higher for the 85/15 feed stock.

Introduction

Secondary sludge is the settled residue accumulated in a secondary clarifier during the wastewater treatment process. Dewatered secondary sludge is one of the solid waste streams in a kraft pulp/paper mill. Because it is a waste, it becomes necessary for a kraft mill to select a disposal method for its dewatered secondary sludge stream. Currently, landfilling is the most popular disposal option. Tipping fees, hauling costs, and special landfilling requirements of hazardous sludges are major drawbacks to landfill sludge disposal. Alternative sludge disposal methods include addition of sludge to recovery boilers, land application, incineration, and lagooning. Although land-applied sludge nourishes vegetation, conditions soil, and helps break down pesticides, disadvantages exist. Hauling costs, land availability, dilution costs, odor problems, and ground water leaching are a few major problems associated with land application. Incineration significantly reduces the amount of material to be landfilled and recovers a portion of energy from the combusted biomass; however, the process produces a flue gas stream containing NO_x, SO_x, and organic halide compounds that must be captured and treated if produced in quantities that exceed permit levels. Other methods of disposal are promising but remain unproven. A sludge disposal method not currently being utilized is sludge addition to a gasification unit (Scott, 1995).

Gasification of black liquor is a relatively new technology and can be used in place of recovery boilers in kraft mills. Gasification is the process of burning a substance in the presence of insufficient amounts of oxygen, producing combustible fuel gas. In a typical recovery boiler setup, heat from the combustion process is captured to produce steam. A steam turbine produces electricity from the steam. Steam is produced in

gasifier systems, as well. However, if gasification is performed under high pressure, the

fuel gas produced can be used to drive a gas turbine, which provides an additional source

of electricity. Therefore, more electricity can be produced per unit mass of black liquor

consumed in a gasification process than from combustion in a recovery boiler. Also, the

possibility of smelt-water explosions is eliminated when gasifiers are used in place of

recovery boilers. Another significant advantage of gasification of black liquor over

traditional combustion is the ability to separate sulfur and sodium. The gasification of

black liquor produces a fuel gas stream and a condensed stream that contains the sodium.

During gasification, a large fraction of the sulfur is volatilized and exits with the fuel gas.

The sulfur in the fuel gas is captured and can be used to produce polysulfide pulping

liquors or kraft liquors with varying sulfidity. This allows for the opportunity to utilize

more advanced pulping methods in mills that use a gasifier in their recovery process

(Frederick, 1999).
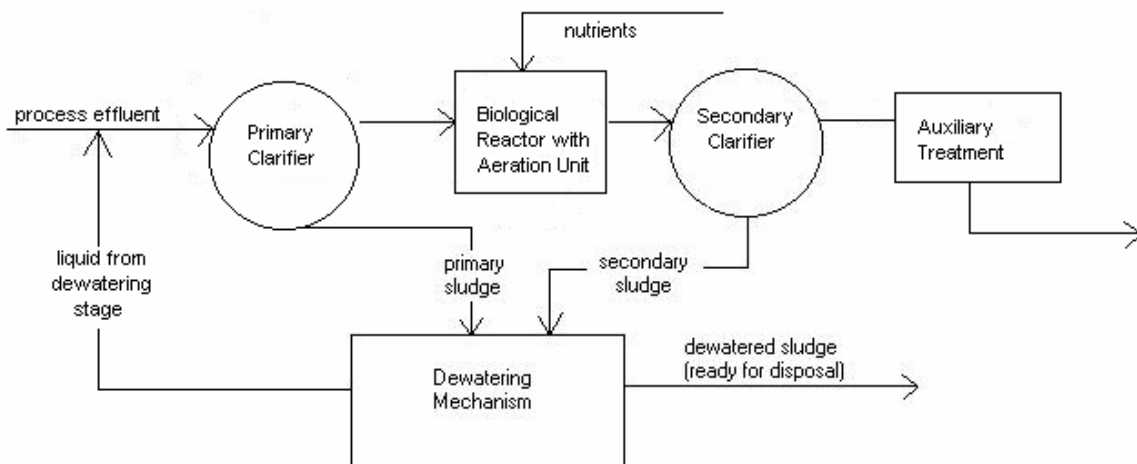
Literature Review

<u>Sludge</u>

Figure 1. Flow diagram of a typical wastewater treatment process (Schwanz, 1999)

'Sludge' is the term applied to the residue generated from the treatment of wastewater streams. Gravity settling is one method used to separate solids from the liquid portion of the wastewater stream. Settling occurs in clarification basins arranged in series within the treatment process. Primary clarification recovers the insoluble portion of the wastewater entering the treatment process. Depending on the nature of the wastewater stream, insoluble solids can account for 1.5% to 6.5% of the raw wastewater composition (Scott, 1995). 'Primary sludge' is the term given to the settled solids accumulated in primary clarification. The liquid portion of the raw effluent stream overflows out of the primary clarifier and enters the secondary treatment process.

In secondary wastewater treatment, bacteria aerobically digest the liquid effluent stream exiting the primary clarifier, reducing soluble BOD (biochemical oxygen demand) and increasing insoluble bacterial biomass. This insoluble biomass is separated from the

liquid portion of the secondary effluent in the secondary clarifier. The solids

accumulated in the secondary clarifier make up 'secondary sludge'.

After exiting the secondary clarifier, the liquid effluent may go through auxiliary

treatment where any soluble toxins are removed to permitted concentrations. Cleaned

effluent is then released to the environment.

Primary sludge runs about 4% solids, while secondary sludge contains about 1%

solids. Typically, primary and secondary sludges are mixed after being pumped from the

clarification units. The mixed sludge is then dewatered, making it ready for disposal.

Primary sludge is generally easier to dewater than secondary sludge, hence the mixing of

the two prior to disposal. Liquid extracted from the sludge dewatering process is

recycled back to the raw inlet stream.

In a typical kraft mill, around 58 kilograms of dewatered sludge is produced per

ton of pulp. Sulfite mills produce sludge on the order of 102 kilograms per ton of pulp.

Deinking mill sludge production is around 234 kilograms per ton of pulp (Scott, 1995).

In addition to organics, sludge contains ash, the inorganic portion. Toxic sludge

components such as cadmium, chromium, and heavy metals are present in parts-per-

million amounts. The following table lists elemental compositions and heating values of

various paper industry sludges. Bark and wood chip data are given for comparison

(Scott, 1995).

Table 1. Elemental compositions and heating values of bark, wood chips, and various sludges (Scott, 1995)

Source	Solids	Ash	C	H	S	O	N	Heating Value (MJ/kg)
Bleached Pulp Mill	33.4	1.9	48.7	6.6	0.2	42.4	0.2	20.1
Typical Pulp Mill	42.0	4.9	51.6	5.7	0.9	29.3	0.9	21.5
Kraft Mill	37.6	7.1	55.2	6.4	1.0	26.0	4.4	24.1
Kraft Mill (2nd Source)	40.0	8.0	48.0	5.7	0.8	36.3	1.2	19.8
Deinking Mill	42.0	20.2	28.8	3.5	0.2	18.8	0.5	12.0
Deinking Mill (2nd Source)	42.0	14.0	31.1	4.4	0.2	30.1	0.9	12.2
Recycle Mill	45.0	3.0	48.4	6.6	0.2	41.3	0.5	20.8
Bark Alone	54.0	3.5	48.0	6.0	0.1	42.1	0.3	20.3
Bark Alone (2nd Source)	50.0	0.4	50.3	6.2	0.0	43.1	0.0	20.8
Wood Chips	79.5	0.2	49.2	6.7	0.2	43.6	0.1	19.4

As evidenced by Table 1, sludges with higher ash compositions have lower heating values. Sulfur content is relatively high in Kraft mill sludge. Sulfur content tends to be higher in pulp mill sludge than in paper mill sludge. The heating value of kraft mill sludge makes it as efficient an energy source as bark or wood chips, based solely on energy produced per mass of fuel burnt. Typical black liquor has a heating value of around 13.4 to 15.5 MJ/kg. Table 1 indicates slightly higher values for paper mill sludges.

Sludge, a derivative of mill wastewater, contains quantities of virtually all of the compounds found in a liquid effluent stream. These compounds are introduced to the effluent by pulping/bleaching reactions, process additives, and pipe corrosion. Ballast compounds, inert effluent compounds that arise from the closing of mill processes, tend to accumulate in pulp and paper mill process loops. Some of these compounds may slowly exit with sludge over time. The following table summarizes the elemental compositions of a variety of pulp and paper mill sludges (McGovern, 1983):

Table 2. Composition of various combined pulp and paper mill sludges on an oven-dried basis (McGovern, 1983)

Element	Average	Range
Macro-wood elements (%)		
N	2.9	0.14-4.1
P	0.34	0.125-0.58
K	0.137	0.037-0.595
Ca	2.95	0.266-9.02
Mg	0.065	0.011-0.100
Micro-wood elements (ppm)		
Fe	2,930	675-7,162
B	13.3	8.5-21.1
Cu	67.4	2.2-90.9
Zn	127.0	41.3-213.6
Mn	119.0	22.9-286.4
Mo	6.7	5.2-8.9
Other elements (ppm)		
Na	0.173 (%)	0.049-0.412
Al	19,500	15,000-22,000
Cd	3.9	1.6-9.4
Cr	39.6	29.2-55.8
Pb	81.9	37.8-129.3
Hg	3.9	3.9

Nitrogen is an essential growth element in wood. However, in pulp mills, about twice as much nitrogen with sludge than enters with wood. This is due primarily to the addition of nitrogen into the effluent treatment process as a bacterial nutrient. According to the McGovern, et al. study, nitrogen makes up about 2.9% of combined sludge. Since nitrogen, on average, constitutes only about 0.13% of black liquor, there is concern that gasifying black liquor mixed with sludge could produce elevated NO_x levels compared to those produced from gasification of black liquor alone (Frederick, 1999).

Phosphorus is also essential for plant growth, and is thereby present in wood entering the pulping process. If phosphorus-containing detergents are used in the pulping process, the amount of phosphorus exiting the mill with sludge can be more than twice

the amount entering with wood. Potassium mostly enters the pulping process with incoming wood. A significant quantity of potassium is added to the effluent in the bleaching process, as well. Typically, about one-quarter of the potassium entering the pulping process with wood exits as sludge. Even though calcium is the most abundant mineral found in wood, about twice as much calcium exits pulp mills with sludge than enters with wood. This is due to the fact that very large quantities of calcium are added in the pulping and bleaching processes. An appreciable amount of magnesium is present in incoming wood. Not much more is added in the pulping process except in the case of magnefite pulping (McGovern, 1983).

Though iron is present at low levels in wood, its concentration in pulp mill sludge is fairly high due to ions introduced through pipe corrosion. Manganese is also contained in low quantities in wood. It remains in even lower quantities in sludge. Manganese is not appreciably added in any part of the pulping/bleaching process, and much of what is present is absorbed by the pulp. Zinc follows much the same pattern as manganese, existing in small quantities in wood and in even smaller quantities in sludge (McGovern, 1983).

Cadmium is a plant toxin and is found in very trace amounts in pulp chips. However, it can enter the pulp mill with detergents, pigments, and plastic/PVC tubing. Because of its tendency to concentrate in sludge, cadmium levels have been regulated in sludge used in agricultural applications. Copper and aluminum both exist as trace elements in wood. Copper ions are continually added in pulping and bleaching processes through corrosion but never reach an appreciable amount in sludge. Aluminum, on the other hand, is present in paper mill effluents in very large amounts from use of clay

coatings and alum. As a result, the aluminum content in paper mill sludges is quite high.

Sodium is moderately contained in wood chips but is added in significant amounts

through kraft chemical make-up and bleaching. Although pulp absorbs large quantities

of sodium, about twice as much sodium leaves with sludge than enters with wood. The

pulping/bleaching process has been shown to either increase or decrease lead quantities in

mill effluents. Mercury levels stay relatively constant when comparing mercury entering

with wood and mercury exiting with sludge (McGovern, 1983).

Impacts of Secondary Sludge Addition on the Recovery Cycle

Adding any non-process element to a kraft recovery cycle raises the concern of

the potential negative effects that the element may have on the pulping and/or recovery

processes. Because secondary sludge is so difficult to dewater, adding it to a black liquor

gasifier may increase the amount of water in the recovery process. Inorganic non-process

elements are inevitably added to the recovery cycle upon introduction of sludge to a

gasifier. The following table details these additions for a sludge incineration scenario:

Table 3. Input rate of non-process elements to a kraft recovery system (15 kg dried sludge solids per air-dried metric ton of pulp at 5% solids addition) (Frederick, 1980)

	Input of Non-Process Elements (kg/air-dried ton)					
Source	Al	Ca	Cl	Mg	P	Si
Mill I Sludge	0.23	0.11	0.03	0.08	0.07	0.10
Mill II Sludge	0.33	0.20	0.005	0.12	0.24	0.23
Mill III Sludge	0.39	0.09	0.005	0.14	0.18	0.59
Mill IV Sludge	1.73	1.78	0.07	0.16	0	1.13
Wood and Makeup Chemicals[a]	0.06	2.46[b]	1.08	0.53	0.2[c]	1.26

[a] from Keitaanniemi, O., and Virkola N.E. except for phosphorus (*Paperi ja Puu* 60(9): 507 (1978)
[b] excluding makeup lime
[c] estimated from phosphorus content of wood (Magusson, H., Mark, K., and Warnqvist, B. *1979 TAPPI Pulping Conference Proceedings*, TAPPI Press, pp. 77-83.)

Adding sludge at 15 kilograms per air-dried ton of pulp in an incineration scenario

increases aluminum content by about ten times. Calcium, magnesium, phosphorus, and

silica levels increase by 10 to 100 percent. The increase in chlorine is less than 10

percent. Calcium, magnesium, and phosphorus leave the recovery cycle as green liquor

dregs. Both chlorine and aluminum are not easily removed from the recovery cycle.

Failure to remove these elements will result in their accumulation within the recovery

cycle. Accumulation of aluminum could cause evaporator fouling, while accumulation of

chlorine can accelerate corrosion problems. Silica is moderately difficult to remove from

the recovery process, but may in part be removed through dregs and grits purges.

Residual silica can build up in the lime cycle, where an added lime mud purge may

become necessary (Frederick, 1980).

Addition of sludge directly to a black liquor evaporator can cause reduction in

evaporator performance. Sludge reduces the heat transfer coefficient of black liquor and

can also leave a slimy deposit on evaporator tubes, further reducing heat transfer.

However, sludge predigested with white liquor is shown to have a minimal impact on

black liquor heat transfer coefficient (Frederick, 1980). Pertaining to gasification of

sludge, evaporator issues arising from sludge itself would probably not come into play

because sludge would be both gasified and digested with white liquor prior to being

evaporated as black liquor. Sludge constituents, however, may cause tube fouling or

other detrimental evaporator conditions over time. These same implications are cause for

concern when sludge is added to a recovery system utilizing a recovery boiler.

Sludge Disposal Methods

Because sludge is a waste, a suitable disposal method must be chosen to keep it

from accumulating. Currently, landfilling is the most popular option. Landfilled sludges

need not undergo father processing after dewatering. Per the normal, a waste contractor

is hired to come to the site and transport the sludge from the mill to the landfill. Sludge

can be landfilled at either mill-owned facilities or independent sites. If an independent

landfill is used, a tipping fee is charged to the mill per ton of sludge hauled away.

Tipping fees vary drastically from rural to metropolitan areas within the United States. In

1993, fees ranged from $7 per ton in North Dakota to nearly $100 per ton in New Jersey

(Scott, 1995). Because of tougher environmental regulations and public outcry, new

landfills are becoming increasingly more difficult to site and build, while existing landfill

space is ever on the decrease. Some sludge streams contain toxic substances in quantities

that render them as hazardous wastes. Hazardous wastes must be landfilled at special

sites that are quite expensive to use relative to non-hazardous landfills. These facts

demonstrate increasing costs associated with landfilling sludge. The following figure

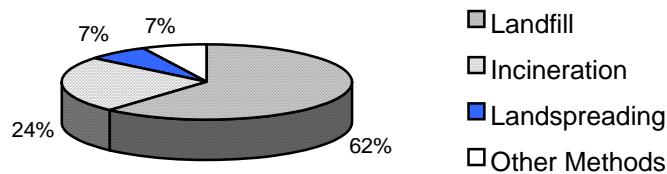represents the popularity of the sludge disposal methods currently used:

Figure 2. Percentage of mills using a given sludge disposal method (Scott, 1995)

As seen from Figure 2, the most popular alternative to landfilling is incineration. No

energy reclamation occurs when sludge is landfilled; however, when sludge is burnt, a

certain portion of energy can be captured from the heat that evolves from the combustion

reaction. Incineration reduces the solid portion of the sludge to ash, thereby decreasing

tonnage that requires landfilling. Incineration is a known and proven technology that can

be trusted. However, certain limitations do exist when this technique is applied to sludge.

Because of its high moisture and ash contents, sludge is not easily kept within its proper

incineration temperature range. Often, modifications have to be made to already

expensive incineration equipment to allow for adequate incineration temperatures.

Modifications may include raising combustion air temperature, removing economizer

surface area, or covering lower furnace walls with heat-refractory materials (Scott, 1995).

Because operating temperatures are lower than traditional traveling-grate incineration

systems, fluidized beds can also be used if sludge composition presents a problem. Due

to the low operating temperatures required for fluidized bed systems, less vaporization of

material occurs and less fly ash is formed. In addition, fly ash on the bottom of the bed

has less tendency to become molten. Both are advantages of fluidized bed systems.

Although high-temperature incineration is good for destruction of chlorinated organics in

sludge, the process also produces undesirable gases such as NO_x and SO_x, as well as

organic halides (Scott, 1995). As air pollution regulations get more stringent, increased

processing of these off gases will be required. This will decrease cost-effectiveness of

sludge incineration processes.

Supercritical water oxidation is an unproven method that has not been applied to

large-scale industrial processes. However, this method shows promise for disposal of

sludge. Bench-scale experiments have shown that a wet oxygen medium can effectively

oxidize sludge at a pressure of 25.5 MPa over a temperature range of 400°C to 600°C

(Scott, 1995). Sludge is mixed with pure oxygen at a 16:1 ratio and is heated in a

pressurized reactor until all of the thoroughly mixed oxygen and organic material are in

the vapor phase. The wet oxygen is allowed to oxidize the sludge into carbon dioxide

and inorganic acid at a residence time of around 5 to 10 minutes. The product mixture is

cooled to room temperature with a heat exchanger. The resulting liquid phase contains

all of the inorganic acids and unoxidized sludge residue, along with a portion of the

carbon dioxide product. The gas phase contains the remaining carbon dioxide and any

unreacted oxygen. These two components are separated and the oxygen is recycled back

to the process. Reduction of total organic carbon can be as high as 99% to 99.9% in the

laboratory. Residual dioxin in the sludge can be reduced by as much as 95% according to

the experiments described by Scott, et al (1995). Energy recovered as steam approaches

45% of the sludge's heating value. This energy recovery and the recovery of carbon

dioxide make the process cost-effective in theory. Initial indications suggest that mill-

scale costs associated with this system could be justifiable. Supercritical water oxidation

requires no dewatering of sludge and produces no odor or any other detectable

environmental problems. Because the oxidation reaction is exothermic, the process,

minus startup, is self-sustaining. Also, residual filler can be separated and recovered

from the inorganic acid stream. However, the technology has yet to be proven reliable

for sludge disposal on an industrial scale (Scott, 1995). Scott, et al list no other potential

disadvantages for this method of disposal.

A lower-tech method of sludge disposal is microbiological degradation through

composting. Sludge is dewatered and put into long rows on the ground. This requires

that a large amount of land space be available. Mechanical aerators travel down the

sludge rows and turn the mass over to ensure aerobic degradation. Alternatively,

machines that force air into the sludge piles can be used in place of compost turners.

Sludges with a wide range of compositions are suitable for composting. Composted

secondary sludge yields material well suited for plant growth, but the presence of heavy

metals may limit a sludge or a sludge residue to nonagricultural uses (Scott, 1995).

Capital expenditure for composting is minimal. However, long degradation times are

necessary to complete the composting process. Other microbiological degradation

methods involve using fungi to remove color from bleach plant effluent and using

bacteria to reduce sludge mass. The latter method produces a high-value protein suitable

for production of animal feed (Scott, 1995).

Another low-tech method of sludge disposal is land application. Typical land

application techniques involve spraying non-dewatered or re-watered sludge onto an

agricultural site or forest floor. When non-dewatered sludge is used, extra hauling costs

allow the sludge to be transported only over short distances. Re-watered sludge refers to

the practice of diluting dewatered sludge at the site of application. Maximum tonnage-

per-area rates exist for land application of wastes. Therefore, aside from transport costs,

land availability is the major obstacle for the process to overcome. There is often a

significant odor, diminishing after about 30 days, involved with the applied sludge.

Heavy metals from kraft pulp mill sludges are usually not present in quantities large

enough to be of concern during land application. However, deinking and wastepaper mill

sludges may have heavy metal concentrations high enough to render the sludges

unsuitable for land application. Other trace materials found in mill sludges, such as

PCBs, organic halides, and chlorinated lignin derivatives, must be addressed before land

application can be approved. These materials will bioaccumulate in plant tissues if

contained in applied sludge (Scott, 1995). Land-applied sludges nourish, condition, and

buffer the soil against pH changes. Secondary sludge, because of its relatively high N:C

ratio, can positively effect the growth of plants. High-ash sludges can improve the
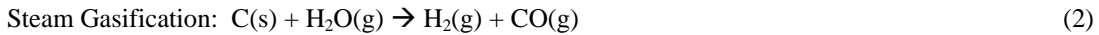
quality of sandy soils by increasing water retention. Land-applied sludge is also useful in

reconditioning strip-mined sites to promote growth of vegetation (Scott, 1995).

Sludge has many other uses that should not be overlooked. More than half of all

recycled paperboard manufacturers in the United States use primary sludge directly as a

filler material. Increased sheet density stemming from increased ash content of process

water, coupled with increased retention aid usage rates are problems resulting from the

disposal of primary sludge by this method. Nitrogen-supplemented sludge has been used

as livestock fodder. Sludge has been used in cement tiles to increase plasticity while

maintaining strength properties. Sludge has also been used as an asbestos substitute and

as a bedding material for cattle.

Gasification

Traditionally in kraft pulping, a recovery boiler is used to burn concentrated black

liquor. This combustion process separates the black liquor into a gas and a smelt stream.

The smelt stream contains the sodium compounds that, when added to water, become the

green liquor that is recycled back into the chemical recovery process. Gasification, by

definition, is the process of reacting a solid with a gas to produce a gas (Whitty, 1997).

Gasification of black liquor produces two streams similar to those resulting from black

liquor combustion. Specific characteristics of the streams produced by combustion and

gasification are somewhat different, however.

Two reactions characterize carbon gasification. Both reactions convert solid

carbon to carbon monoxide. Steam gasification reacts solid carbon with water to produce

hydrogen gas as a byproduct. Carbon dioxide gasification reacts solid carbon with

carbon dioxide, producing only carbon monoxide.

Combustion: $C(s) + O_2(g) \rightarrow CO_2(g)$ (1)

Steam Gasification: $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$ (2)

Carbon Dioxide Gasification: $C(s) + CO_2(g) \rightarrow 2CO(g)$ (3)

Combustion is an exothermic reaction that is self-sustaining provided that access to oxygen is adequate. In fact, the reaction is exothermic to the degree that the burning of black liquor in a recovery boiler is a major source of energy for kraft mills. Both gasification reactions outlined above are endothermic, and heat must be provided to sustain them. Providing heat and the necessary steam and carbon dioxide to drive gasification may seem very costly compared to recovery boiler combustion, in which nothing needs to be added except air to sustain reaction. However, it is possible to produce more electricity from the gasification process than can possibly be produced from recovery boiler combustion on a per-weight black liquor basis (Whitty, 1997).

The entire black liquor gasification process can be divided into three steps. Black liquor is introduced to the gasifier in droplet form. The first step in gasification is drying of these droplets. Drying involves simply removing water from the black liquor droplets. Heat transfer controls the rate of droplet drying. If the time required to bring the droplets up to the water evaporation temperature is minimized, droplet drying rate will be maximized. Smaller droplets will dry more quickly than larger droplets. Black liquor droplets typically dry in less than one second. The drying process causes the droplets to swell to about 1.5 times their original size.

The second step in the overall gasification process is pyrolysis of the dried droplets into char particles. During pyrolysis, organics contained in the droplet degrade into gaseous compounds. Carbon dioxide and carbon monoxide, hydrogen, light

hydrocarbon gases, and sulfur gases are formed. Heavier hydrocarbons called tars are also formed and then converted into lighter species. Pyrolysis reactions typically take less than one second to occur. Their rates are heat transfer-controlled similar to the drying phase rate. Significant swelling takes place during pyrolysis, resulting in droplets increasing more than 30 times in diameter. The char produced in the second step contains the non-volatile organic material and most of the inorganics present in the original droplets.

The final step in gasification is called char gasification. In this step, organics in the char are transformed into gaseous species through equations (2) and (3) listed above. The rates of the gasification reactions determine the overall rate of this step, which takes longer to complete than the first two. Reaction rates are extremely sensitive to temperature, and the transport rate of gases to the char particle reaction sites becomes the limiting rate factor at temperatures above 1100°C. Char particles shrink dramatically during the third step and are transformed into inorganic smelt (Whitty, 1997).

In addition to the reactions of the organic species, some inorganic decomposition is observed. Sodium carbonate and sodium sulfate are the two inorganic compounds whose degradations are most noteworthy. The following reactions demonstrate each species' method of decomposition:

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO \tag{4}$$

$$Na_2CO3 + C \rightarrow 2Na + CO + CO_2 \tag{5}$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO \tag{6}$$

Generally, these reactions take place during the char gasification stage. However, they will occur anytime the liquor is exposed to relatively high temperatures for an extended period of time (Whitty, 1997).

To make gasification commercially feasible for use as a recovery boiler alternative, engineering must be employed to overcome gasification's inherent disadvantages, namely its endothermic characteristics and its supply requirements of carbon dioxide and water. The problem of water input solves itself in the case of black liquor, as the droplet drying stage supplies the necessary quantity of steam. Before gasification begins, the incoming black liquor is allowed to burn in the presence of insufficient amounts of combustion air. The air is fed at the correct stoichiometry, and reacts with black liquor to produce carbon dioxide to meet the supply needs of the gasification reaction. The gasification reactions produce a flue gas that combines hydrogen and carbon monoxide. The flue gas is cleaned free of particulates after exiting the gasifier. After cleaning, these gases are combusted and heat is generated. Integrated combined cycle gasification schemes gasify reactants under pressure. This pressure is used to drive a gas turbine to produce electricity. The products are then passed through a standard heat recovery boiler where steam is produced. Steam is routed to a steam turbine where further electricity is generated. Through the use of this type of energy recovery process, the electrical/thermal ratio of gasification can be more than double the same ratio for a traditional recovery boiler (Whitty, 1997).

Today, there are two types of gasification systems that can be applied to black liquor conversion. Entrained-flow gasifiers operate above the melting temperature of the sodium/sulfur compounds produced during gasification. The product is quenched with an

aqueous solution to separate the product gases from the smelt. The smelt components are dissolved and recovered. This is the process that has been applied industrial pilot scale to the black liquor produced in kraft pulping. The second type of system uses a fluidized bed as the gasifier. These units operate below the melting temperature of the smelt stream salts. In this process, inorganic solids and residual char are continuously removed from the bed and dissolved for recovery (Frederick, 1999).

Black liquor gasification diverts a large quantity of the sulfur in the reaction products to the fuel gas stream. This allows generation of a smelt with low sulfur concentrations relative to smelt from traditional combustion, especially at lower temperatures. Upon pyrolysis, virtually all of the sulfur, except sulfate, becomes part of the fuel gas. At high temperatures, some of this sulfur recombines with the sodium salts present to form condensed sodium sulfide. Gasification offers the opportunity to recover sulfur from the hydrogen sulfide captured in the fuel gas stream instead of recovering sulfur exclusively from smelt. Hydrogen sulfide can be readily scrubbed from the fuel gas stream for sulfur recovery purposes. Furthermore, recycling of pressurized hydrogen sulfide back to the gasifier after capture allows for control of the sodium sulfide (smelt sulfur)/hydrogen sulfide (fuel gas sulfur) ratio. This allows flexible separation of the sodium/sulfur compounds. This is an advantage when applied to more advanced pulping methods such as minisulfide sulfite anthraquinone (MSSAQ) and alkaline sulfite anthraquinone (ASAQ) (Frederick, 1999).

Low temperature gasification in a fluidized bed arrangement would be ideal for both ASAQ and neutral sulfite semichemical (NSSC) pulping. Low temperature gasification offers superior sulfur/smelt separation, which is essential in these pulping

systems. When applying the fluidized bed technology, oxygen feed must be tightly

controlled when converting hydrogen sulfide to sulfur dioxide in the sulfur recovery

process. This is due to the fact that sodium carbonate may not reduce effectively during

sulfur recovery in the fluidized bed setup. For magnesium bisulfite pulping processes, a

high temperature gasification unit would be the ideal choice. The temperature should be

above 800°C for the magnesium process to ensure complete gasification of the carbon

(Frederick, 1999).

By most estimations, black liquor gasification has great potential for economic

savings over traditional recovery boilers. Gasifier capital costs may be small compared

to recovery boiler costs. Potential energy savings are promising. A study by Larson, et

al., published in the 1998 TAPPI Chemical Recovery Conference Proceedings details a

cost/benefit analysis for a hypothetical mill utilizing a polysulfide pulping process. Four

chemical recovery scenarios are analyzed: hydrogen sulfide scrubbed with green liquor

and sent to the lime cycle, hydrogen sulfide scrubbed (without green liquor) and recycled

back to the gasifier, polysulfide liquor generation from combination of white liquor and

sulfur dioxide, and full hydrogen sulfide recycle using an air-blown gasifier.

Table 4. Net operating costs for a black liquor gasification system relative to a Tomlinson boiler (Larson, 1998)

Costs (million $/yr)	Scenario 1 (green liq scrub)	Scenario 2 (H$_2$S recycle)	Scenario 3 (polysulf liq gen)	Scenario 4 (full H$_2$S recycle)
Operation/Maint.	11.94	12.19	15.60	4.90
Biomass Fuel	3.49	4.77	4.77	3.82
Natural Gas Fuel	0.11	0.61	1.97	0.58
Kiln Fuel	1.59	----	0.22	----
H$_2$S Scrub Solvent/Catalyst	----	0.10	0.10	0.10
AQ	----	----	1.64	----
Wood Cost	----	----	-2.99	----
Electricity Cost	-29.00	-28.53	-28.69	-16.48
Net Cost	-17.05	-16.34	-16.09	-11.58

As evidenced by Table 3, operation and maintenance costs are high relative to those for a

Tomlinson boiler. However, the electrical savings realized through use of black liquor

gasification are so great, it is estimated that gasification would provide a savings ranging

from about 12 to 17 million dollars per year relative to a Tomlinson boiler for the listed

recovery scenarios (Larson, 1998).

Because gasification has been prevalent for some time in the fossil fuel industry,

much equipment has been developed that can be applied to pulp mill gasifiers. Some of

this equipment needs little to no modification. Such is the case for gas turbines and other

power generation equipment, as they run virtually independently of their fuel source. In

contrast, some equipment is fuel specific, such as particle removal and gas handling

equipment. Of particular interest is heat refractory material within the black liquor

gasifier. Functioning refractory material exists, but life spans under gasification

conditions are largely unknown. Much remains unproven in the area of smelt recovery

for gasifiers, as smelt produced from gasification differs from smelt produced in

conventional recovery combustion. Even if equipment used is already being utilized in

another industry, optimization studies are required for most gasification equipment

installed for the purpose of black liquor conversion (Oscarsson, 1999).

Sulfur Species and Pyrolysis

Pyrolysis and gasification reactions can occur simultaneously. Degree of sulfate,

thiosulfate, and sulfite reduction in the char phase directly affects sulfur product gas

composition. The major sulfurous pyrolysis products are hydrogen sulfide, methyl

mercaptan, dimethyl sulfide, carbon disulfide, and carbonyl sulfide. Upon black liquor

pyrolysis, most of these species have been shown to reach a maximum concentration

relative to temperature and then start to decompose (Brink, 1970; Li, 1989;

Sricharoenchaikul, 1994). Sodium sulfate and sodium sulfite are relatively stable at

temperatures up to 550°C (Strobheen, 1982). Sodium sulfide and sodium thiosulfate

readily volatilize to form sulfur gases. Sodium sulfite, although relatively stable at lower

temperatures, can decompose into SO_2 in the presence of vanillic acid (Brink, 1970). The

following equation illustrates this transformation without the presence of oxygen being

necessary:

$$Na_2SO_3 + 2HA \rightarrow 2NaA + H_2O + SO_2 \tag{7}$$

At black liquor pyrolysis reactions below 700°C, thiolignin and sodium

thiosulfate are the major producers of sulfur gases (Li, 1991). Their decompositions are

detailed below:

$$Na_2S_2O_3 \rightarrow S + Na_2SO_3 \tag{8}$$

$$S + H_2O + CO \rightarrow H_2S + CO_2 \tag{9}$$
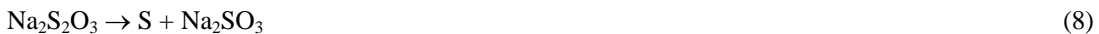
Reduction of sodium sulfate to sulfide only significantly occurs above temperatures of

700°C (Sricharoenchaikul, 1995). Sodium sulfide has the potential to form a variety of

different sulfur compounds.

Early LEFR work at Oregon State University yielded data concerning the

formation and decomposition of sulfur gases upon gasification in the presence of

nitrogen. The following compounds were seen to rapidly form and disappear above

900°C: hydrogen sulfide, dimethyl sulfide, carbon disulfide, carbonyl sulfide, and sulfur

dioxide (Sricharoenchaikul, 1995). Under the same conditions, sulfite was seen to

degrade and sulfide to continue forming. The following reactions were theorized to be

responsible for producing the major sulfur species in the LEFR reactions:

$$Na_2S_2O_3 + CO_2 \rightarrow Na_2CO_3 + SO_2 \tag{10}$$

$$Na_2S_2O_3 + 3CO \rightarrow Na_2S + S + 3CO_2 \tag{11}$$

$$Na_2S_2O_3 + Na_2CO_3 \rightarrow Na_2S + Na_2SO_4 + CO_2 \tag{12}$$

$$Na_2SO_4 + CO \rightarrow CO_2 + Na_2SO_3 \tag{13}$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \tag{14}$$

$$Na_2S + H_2O + CO_2 \Leftrightarrow Na_2CO_3 + H_2S \tag{15}$$

$$CH_4 + 2S_2 \rightarrow CS_2 + 2\ H_2S \tag{16}$$

$$S + H_2O + CO \rightarrow CO_2 + H_2S \tag{17}$$

$$CS_2 + H_2O \rightarrow COS + H_{2S} \tag{18}$$

Due to the tendency of vaporized elemental sulfur to latch onto H-C bonds, a wide

variety of mercaptan compounds are formed in the pyrolysis/gasification process

(Senning, 1972). Decomposition of these species is rapid at temperatures above 700°C,

however (Sricharoenchaikul, 1995). Sricharoenchaikul also discovered that the sulfide

forms faster than the sulfate reduction rate. This has led to structures such as sulfite

being suggested as possible sulfate reduction intermediates.

Reduction of sulfate was found to be first order in respect to the surface area of

available carbon for reaction (Cameron, 1982; Grace, 1985) at moderate temperatures.

Further, alkali carbonates in the char were found to catalyze the reaction. The reaction

was proposed to follow Langmuir-Hinshelwood kinetics, which describe a heterogeneous

reaction where gaseous reactants adsorb, react, and desorb off of a solid substrate.

Pertaining to the reduction of sulfate, it is also suggested that activated, oxygenated sites

are formed from reaction with carbon dioxide. The following equation describes the rate

of sulfate reduction during pyrolysis according to Cameron and Grace:

$$\frac{d[SO_4]}{dt} = \frac{K''[SO_4][C]e^{-E/RT}}{1 + K[SO_4]} \tag{19}$$

where: K, K'' = physical constants
        E = activation energy
        R = gas constant
        T = temperature (absolute)

The model indicates that sulfate reduction is a function of carbon availability and of

sulfate concentration at low sulfate concentration. Frederick, et al has shown the model

to break down at temperatures at or exceeding 1000°C, suggesting a differing rate law

may apply at higher temperatures. Elevated temperatures showed the Cameron and

Grace model to predict sulfate reduction an order of magnitude too low. Further studies

(Sricharoenchaikul, 1995) revealed that sulfite is indeed formed as a reduction reaction

intermediate by the following reaction:

$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2$ (20)

The Cameron and Grace model was modified to take the preceding into account.

Nitrogen Oxide Formation

Four methods are responsible for forming NO_x in the LEFR: nitrogen release; formation from char; formation from volatile nitrogen; and formation from nitrogen in combustion air (Forssen; Iisa, 1998). Nitrogen release from char is accomplished during devolatilization. Devolatilization occurs within the first few tenths of a second of the reaction and is temperature dependent. Temperature increases cause the release of nitrogen to go up, even at post-volatilization times. Nitrogen release also increases with increasing residence time. Devolatilization products are molecular nitrogen, ammonia, and char nitrogen (Forssen; Iisa, 1998). After devolatilization, NO_x can form from oxidized char. NO_x can also be formed from volatile nitrogen. In this scenario, ammonia, the main reactive nitrogen intermediate released during pyrolysis, is oxidized to form NO_x. The fume compounds Na_2CO_3 and Na_2SO_4 catalyze this reaction (Iisa, 1998). Ammonia can also react with NO in the presence of oxygen to form more NO (Iisa, 1998). There is also gas phase oxidation of ammonia, in which ammonia reacts with NO in the presence of oxygen to form NO (Iisa, et al., 1998). Ammonia conversion to N_2 is also possible, according to Forssen, et al (1998). Another study has also shown that recovery boiler smelt can decompose NO into N_2 and O_2 (Thompson, 1995).

Objectives

The goal of this study is to examine the feasibility of gasifying black liquor mixed with kraft mill secondary sludge. Specifically, the experiments addressed the following issues:

1. Although secondary sludge has a relatively high organic content, it may have reduced the heating value of black liquor fuel gas from gasification. This may

have rendered the black liquor fuel gas stream a less efficient source of electricity.
Objective 1 was to compare the components of the gaseous products attained from
gasification of the sludge/liquor mixtures to determine the effects that sludge
addition had on heating value of the feed solids.

2. Secondary sludge may have had an effect on rate of gasification. Objective 2 was
   to compare the organic char recoveries for the gasification of the sludge/liquor
   mixtures to infer relative gasification rates.

3. Secondary sludge has high nitrogen content compared to that of black liquor.
   Therefore, incineration or gasification of sludge may have produced NO_x gases
   that pose environmental concerns. Objective 3 was to compare the generation of
   NO_x precursor levels (ammonia) produced from the gasification of the
   sludge/liquor mixtures.

4. Non-process elements constitute a small fraction of secondary sludge but still may
   affect contents of these components in green liquor produced in the recovery
   process. Objective 4 was to compare the fraction of green liquor NPEs recovered
   for the gasification of the sludge/liquor mixtures.

Experimentation

Scope

The goal of this research was to compare certain characteristics of the products
produced in the gasification of black liquor alone versus those of products produced in
the gasification of black liquor mixed with a quantity of secondary sludge. The
characteristics of concern were organic carbon recovery in the product char stream, sulfur
species content of the product gas stream, fuel gas content in the product gas stream,

ammonia content of the product gas stream, and non-process element content of the

product char. Three experimental variables were considered. They were gasification

time, temperature, and sludge/liquor solids ratio. The sources and compositions of kraft

mill sludge and black liquor themselves were not varied in the experimental work.

LEFR Bench-Scale Gasifier

      The apparatus used for experimental gasification was a laminar entrained-flow

reactor (LEFR). The unit is capable of operating at temperatures comparable to industrial

gasifiers, achieving a maximum temperature of 1150°C (Sricharoenchaikul, 1994).
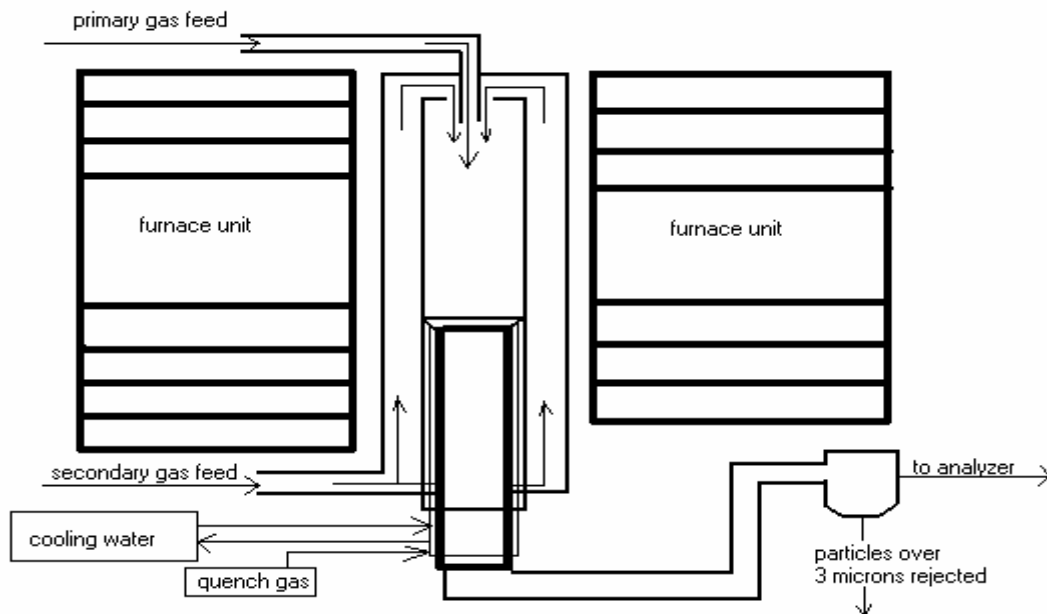
Figure 3. Schematic of the LEFR (Sricharoenchaikul, 1994)

Two tubes of 70 and 90 millimeters inner diameter were concentrically positioned inside

a 36-inch Linberg furnace. Flanges at both ends of the reactor supported the tubes where

gases entered and exited the unit. A water-cooled injection probe fed particles entrained

in a primary flow. A honeycomb flow-straightener maintained laminar flow for the

secondary gas feed. The secondary gas became preheated as it flowed upward to meet

the primary flow. Pre-heating of the secondary gas allowed for near instantaneous

heating of the feed particles upon injection into the reactor. The primary gas was not

preheated. Mass flow meters measured feed gas flow rates. The reactor was designed to

provide a laminar stream of feed particles that flowed down in a tight radius centered

within the inner concentric tube. The laminar particle flow allowed all particles to have

nearly identical residence times. Once particles had moved out of the reaction chamber,

they were quenched in a moveable collector. Two quench gas streams served to cool the

gasified products. The first stream was for rapid cooling of the product particles and

gases. The second stream quenched through the collector walls to prevent particle

deposition on the walls of the collector. Because of the rapid feed particle pre-heating

and the rapid cooling of the particles once they reached the movable collector, reaction

time became nearly equal to residence time. Exiting the collector, particles were passed

through a cyclone with a cutsize of 3 microns. Note that the 'cutsize' was the size at

which 50% of the particles were collected. Rejected particles were collected for solids

analysis, while the accepts stream was filtered to remove the significant quantity of

remaining fine solid particles. Either changing primary/secondary flow rates or changing

collector position changed reactor residence time. Exact positioning of the height of the

movable ceramic collector tube to obtain specific particle residence times was calculated

based on a computer model for entrained particle heating. Relations for the model were

developed by Flaxman, et al (1989). Gas chromatography was used to analyze sulfur

gases in the product gas streams.

Gasification process gases included N_2, CO_2, and H_2O. Run duration was from 5-

10 minutes to ensure that steady-state had been achieved. Secondary gas flows for the

experiments were 75/15/15% nitrogen/carbon dioxide/water on a molar basis. Primary

gas flowed at about 150 ml/min, while secondary nitrogen flowed at about 10.7 liters/min

and CO_2 about 1.27 liters/min. Quench gas flowed at approximately 14 liters/min.

Research grade nitrogen and carbon dioxide were dispensed from pressurized cylinders.

Bubbling the secondary flow through a heated water bath allowed water vapor to enter

the secondary stream. The bath was heated to 40.6°C based on steam table data to ensure

the proper secondary gas molar ratio. The fraction of water vapor in the secondary gas is

given by the equation:

$$y_{H2O} = \frac{p_{H2O}^{sat}(T)}{P_{total}} \tag{21}$$

where: y_{H2O} is the mole fraction of water in the feed gas
 $p^{sat}(T)$ is the vapor pressure of water at the temperature of the water bath
 P_{total} is the ambient pressure.

Dried liquor solids, entrained in the primary flow, were fed into the reactor at

about 0.263 grams/min on average. Wet liquor was mixed to the proper solids ratios,

dried, ground in a jar mill, and sieved to a particle size range of 53-125 microns. The

black liquor used was obtained from Domtar's Woodland, ME, mill (formerly Georgia

Pacific) in 1997. Below is a description of the hardwood black liquor source:

Table 5. Typical Species Distribution of Domtar's Woodland, ME, chip yard

Species	Weight %
Maple	54
Birch	24
Beech	14
Aspen	8
Oak & Others	1

~6% deviation for any species

Total carbon data for the black liquor and 85% sludge feed stocks can be found in the

appendix. Secondary sludge was obtained from Inland Paperboard mill in Rome, GA, in

2002. Below is an elemental analysis taken from Schwanz (1999). The analysis comes

from secondary sludge taken from the same source as the one used for the experiments:

Table 6. Elemental analysis of Inland's--Rome, GA, secondary sludge

Element	Secondary Sludge wt%
C	38.57
H	4.57
N	2.725
O*	48.99
Na**	0
K**	2.98
S**	0.82
Other	1.35

*by difference
**calculated based on metals analysis (Schwanz, 1999)

Experimental Conditions

        The following table lists all experimental variables and levels used in the

experimentation:

Table 7. Experimental Variables

Variable	Levels
Residence Time	0.2, 0.7, 1.2 seconds
Reaction temperature	700, 900 °C
Black Liquor/Sludge Ratio in Feed	100/0, 95/5, 90/10, 85/15

All 24 combinations of the levels were run in duplicate, yielding 48 total experiments. It

was not practical to totally randomize the run order of the experiments. Moving the

collector to change residence time required the reactor temperature to be less than 200°C.

Cooling down from the reaction temperature to this temperature took hours to

accomplish. Even cooling down and heating up the reactor between the two run

temperatures took a long time. Therefore, I blocked the experiments by temperature and

residence time. I ran 4-8 experiments per day at the same temperature and residence

time. The only thing that was randomized was the sludge mixing composition for all runs

on a certain day.

<u>Solid Product Collection</u>

Fume was collected on filter paper with a pore size of 1.2 microns. Most of the

fume was collected on the exhaust end of the cyclone on a 90mm filter. The balance of

the fume was collected on a 47mm filter that prevented particulate matter from exiting

the cyclone via tubing that ran from the cyclone to the chemiluminescence NOx meter.

Inevitably, some of the solid reaction product stuck to the walls of the cyclone. This

material was collected with the char. Because no analysis was performed on the fume

samples, they were mixed with their respective char samples after masses were obtained

for both. Because water vapor was being used as part of the feed gas, heat guns were

used to maintain the cyclone at a high temperature to prevent condensation from forming

inside the cyclone. No problems arose with water condensing inside the cyclone. Char

product in the cyclone was massed and saved after each experiment. Because each of the

24 experiments was performed in duplicate, two char/fume samples per level

combination were collected. Each pair of samples was thoroughly mixed together in

preparation for analysis.

Samples from the collected mixed char and fume were used to determine

carbonate levels in the solid product using the headspace chromatography technique

developed by X.-S. Chai, et al (2000). The IPST analytical lab also analyzed selected

char samples for total carbon, total sulfur, and metals. 100% and 85% black liquor feed

stocks were also analyzed for total carbon, total sulfur, and metals. Total carbon was

determined using a high-temperature combustion/coulometric titration technique. Total

sulfur and metals analyses were carried out using inductively-coupled plasma technology.

Determination of Carbonate in Char/Fume Samples

The headspace chromatography method used to determine carbonate levels in the

char samples was very effective. The theory behind the analysis is that the carbonate

portion of a solid analyte will react with sulfuric acid in a sealed vial to produce carbon

dioxide gas via the following reaction:

$$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O \tag{22}$$

An HP-7694 automatic headspace sampler and a Model HP-6890 capillary gas

chromatograph (TCD detector) were used to measure the amount of carbon dioxide

generated in the vial headspace via the above reaction. Sampler parameters can be found

in X.-S. Chai, et al (1990). 0.1 molar (estimated) solutions of char/fume product were

dissolved in distilled water and injected into 21.6 ml glass vials. The vials were then

capped with butyl septa and injected with 0.5 ml of 2.0 molar sulfuric acid. Four vials of

pure sodium carbonate solution at concentrations of 0.1-0.4 molar were sampled to

generate a calibration curve for the char/fume samples. A blank vial was also sampled to

calibrate for any ambient carbon dioxide in the vials not generated by the acid/carbonate

reaction. The sequence of vial sampling was totally randomized. The carbonate

calibration curve and raw data results can be found in the appendix.

Chemiluminescence NOx Analysis

Nitrogen oxide (NO_x) compounds were analyzed on-line by a chemiluminescence

NO-NO_x analyzer (NO/NO_x Instruction Manual). Chemiluminescence is an analytical

technique that produces wattage proportional to the molar concentration of a gas through

detection of emitted light energy. The analyzer was run with the converter option

activated. This meant that convertible nitrogen products from the gasification reaction

(NO) were converted to excited-state NO_2* molecules in a special converter chamber.

The following details the conversion process:

1. Ammonia was partially converted to NO in during gasification. Molar conversion

   values were calibrated at ~45% at 700°C and ~60% at 900°C based on six

   preliminary experiments. The experiments entailed feeding a quantity of

   ammonia gas with the secondary gas stream into the LEFR minus a feed solids

   stream. Parts-per-million NOx readings were taken on the chemiluminescence

   meter and compared to the feed rate of ammonia entering with the secondary gas

   stream. A molar percent conversion from NH_3 to NO in the reactor for each

   temperature was then calculated. This calibration was also important because

   portions of the ammonia generated in the reactor have a tendency to absorb on

   reactor surfaces and not complete the trip to the NOx analyzer. Furthermore, this

   calibration took into account any ammonia that might get converted to N_2. Dr.

   Iisa's experience was that conversion was fairly independent of ammonia

   concentration.

2. Ozone was generated from pressurized air or oxygen in an ozone generation

   chamber.

3. NO from the converted ammonia entered the conversion chamber and reacted

   with ozone to form excited NO_2* and oxygen. The excited nitrogen compound

   then reverted to its ground state and emitted a light-producing photon. A photo-

   multiplier tube detected the energy emitted and generated a wattage signal. This

signal was directly proportional to the molar concentration of NO_x in the sample

gas. The converter reactions are detailed below:

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad\qquad (23)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad\qquad (24)$$

The wattage was calibrated for NO concentration with a standard cylinder of NO.

Gas Collection and Analysis

Gas samples were collected one time per experiment after the reaction time had

reached 2 minutes. Samples were collected with a valved Tedlar bag and immediately

taken to an oven set at 60°C with its door left open. The bag sat on a Teflon pan until it

was ready to be sampled. This was done to prevent any existing moisture from

condensing inside of the bag. Two samples per bag were taken for chromatographic

analysis. Because each level combination was duplicated, four sets of outputs were

obtained per level combination. Integrated areas from the four were averaged for each

level combination. The averages were compared to the calibration graphs specific to

each gas species to determine ppm concentration amounts. All calibration curves yielded

linear trend lines with R^2 values over 0.99. Calibration curves were generated from

specialty sulfur gas mixtures of known concentrations in nitrogen. One calibration

mixture containing the three larger mercaptans considered was over two years old, calling

into question the accuracy of its stated concentrations. The standards used for the other

species were all less than a year old. The following sulfur compounds were analyzed for

content in the experimental product gases: COS, CS_2, H_2S, methyl mercaptan, ethyl

mercaptan, n-propyl mercaptan, and isobutyl mercaptan. CS_2, ethyl mercaptan, and

isobutyl mercaptan were present in levels small enough to be disregarded. Therefore,

only COS, H_2S, methyl mercaptan, and n-propyl mercaptan results were acknowledged.

In addition, it was desired to measure for dimethyl sulfide, but the quality of calibration

gas that was obtained became questionable. Information concerning dimethyl sulfide

generation from LEFR gasification can be found in (Horenziak, 1999).

Gas samples were analyzed using an HP 5890 Series II gas chromatograph. Peak

integration was performed using HP Chemstation software. A 30-meter GS-GasPro

capillary column from J&W Scientific was used for sulfur gas analysis. Table 8 shows

the parameters used for operation of the chromatograph.

Table 8. HP 5890 Series II GC operating parameters for sulfur analysis.

Parameter	Values
Detector	TCD, 210°C
Injection	Capillary, splitless, 200ul, 220 °C
Oven Temperature Program	31°C for 5 min., 31-200°C 10 C/min, 200°C hold for 8 min.
Column head pressure	Approximately 12 psig, resulting in 3.3 ml/min
Reference flow	17 ml/min
Make-up flow	2.6 ml/min
Purge Vent flow	50 ml/min

Peaks generated for each gas were of reasonable deviation. Although of

reasonable error margin relative to one another, the individual integrated area results

seemed to drift from day to day with respect to H_2S. H_2S did not follow the downward-

with-temperature trend that theory predicted. H_2S was the only gas that seemed to trend

with the days the chromatograph was used. This trending may have been why the data

generated for H_2S did not follow theory. An additional source of error may have been

feed rate variations during the experimental reactions. This had been noted as a problem

in previous LEFR work. It was because of this that the Tedlar bags were used for

collection as opposed to glass sampling bulbs. The bags had a much greater capacity

than the bulbs, which allowed sampling to be performed continuously for many minutes.

This was intended to lessen the impact of feed rate variation throughout a particular

experiment. The Tedlar bags themselves might have caused some problems, however.

Only a small number were available, so they were continuously reused. Contamination

from sample to sample due to reuse of the bags was a concern. Each bag was filled and

emptied three times with nitrogen in attempts to 'rinse' it clean before each use.

However, some residual gas may have remained to contaminate the next sample taken.

Also, since the bags were well worn, small leaks may have developed in the valve portion

where the sampling needle was injected. It probably would not have been a problem if

gas had simply leaked out; however, any gas exchange with the ambient air would cause

error in the analyses for that particular bag of gas.

Data Analysis

Weights of the solid feed samples were taken before and after each run. Reaction

times were measured to determine the solids feed rates. Char and fume samples were

weighed after each experiment so that a percent solids recovery could be calculated.

Char recoveries were calculated on a mass basis. Recoveries for sulfurous gas species

were calculated on a molar basis according to the following formula:

$$R_x = \frac{(C_x)(Q + P + S)(v)}{F_s} \tag{25}$$

Where: R_x = the fractional recovery of feed sulfur as species x, unitless
C_x = mole fraction of species x in the gaseous product
Q = the molar flow of quench gas (mol/min)
P = the molar flow of primary gas (mol/min)
S = the molar flow of secondary gas (mol/min)
v = moles of elemental sulfur per mole of species x
F_s = molar feed rate of elemental sulfur to the reactor (mol/min)

The molar fraction of a particular sulfur species (C_x) is simply the ppm value calculated from the chromatograph calibration curve divided by 10^6. The molar feed rate of elemental sulfur was determined by the solids feed rate multiplied by the weight fraction of elemental sulfur in the solid feed (from metals analysis). Because of cost, only the 100/0 and 85/15 feed stocks were measured for total sulfur. Therefore, total sulfur values for the 95/5 and 90/10 feed stocks were interpolated using the already measured values. Using the above equation eliminated feed rate variation as a consideration from experiment to experiment. It did, however, assume a constant feed rate for each particular experiment, at least during the duration that the product gas sample was being taken. This assumption was not always valid and contributed to some experimental error.

Initially, FTIR analysis was going to be used to measure the carbonaceous fuel gas components in the product gas (i.e. CO and CH_4). However, the FTIR that had been housed in the IEC had been relocated. Therefore, it was decided to attempt to measure CO, CH_4, and H_2 (additionally suggested) with the same chromatograph and column with which I wanted to measure sulfur species. This turned out to be a fruitless proposition, however, as the large nitrogen peak that was generated upon chromatographic analysis literally enveloped the CO, CH_4, and H_2 peaks. Through talking to an Agilent technician, I was able to determine that the only way that I could effectively separate these three problem species with the column that I had was to attempt cryogenic chromatography. Unfortunately, I had neither the time nor the budget to undertake this. Therefore, an equilibrium simulation was carried out at 900°C and 1.2 seconds residence time to attempt to estimate levels of CO, CH_4, and H_2 generated for the 100/0 and 85/15 feed mixtures.

Results and Discussion

Process Simulation

        The equilibrium process simulation was made on HSC Equilibrium Calculation software. The software was a bit primitive in that it only allowed iteration by one of three things: amount, temperature, and pressure. Furthermore, iteration could only be performed for one of the above parameters at a time. From Sricharoenchaikul, et al (1994), a particle heating versus time graph for equilibrium temperatures of 700 and 900°C was generated:
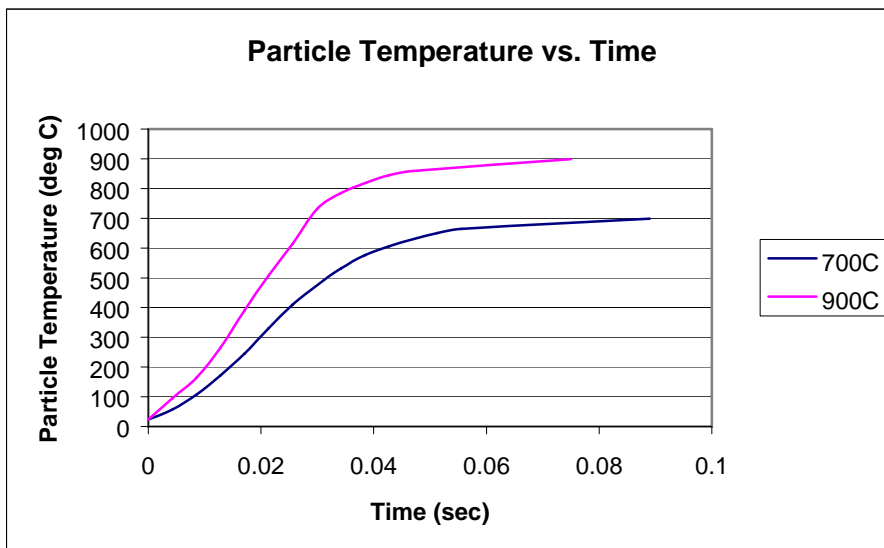

Figure 4. Particle temperature vs. time for a LEFR (Sricharoenchaikul, 1995).

Once the curves were generated, trend lines were fit to them for use in a calculation spreadsheet. For the simulation to function, it required input of all species that might be either fed or formed. Initially, an attempt was made to input black liquor organic components based on molecular structure. This, however, did not work since the simulator would not accept complex chemical formulas as inputs. Accordingly, a list of all of the CHO compounds that were valid in the eyes of the simulator was made.

Microsoft's Excel solver was used to distribute the feed quantities of these various

chemicals to most closely match elemental analyses for both 100/0 and 85/15 feed stocks.

The elemental amounts were matched up to elemental analyses obtained by Schwantz

(1999). The following table illustrates the Schwanz analyses:

Table 9. Elemental analyses for black liquor and secondary sludge mixtures (Schwantz, 1999).

Element	% in 100/0 BL/Sludge	% in 85/15 BL/Sludge
Carbon	32.2	33.1
Hydrogen	3.21	3.41
Nitrogen	0.07	0.47
Oxygen	36.5	38.3
Sodium	20.5	17.4
Potassium	3.04	3.03
Sulfur	4.46	3.91
Other	0.58	0.70

The following table completely breaks down what was inputted as feed into the simulator

for each feed composition:

Table 10. Feed components for LEFR gasification simulation.

Gas Components (100/0)	grams	Gas Components (85/15)	grams
N_2	12.481	N_2	12.481
CO_2	1.710	CO_2	1.710
H_2O	0.700	H_2O	0.700
BL Components (100/0)	**grams**	**BL Components (85/15)**	**grams**
$C_8H_8O_2$	0.00024027	$C_8H_8O_2$	0.0102541
$C_8H_6O_4$	0.048960324	$C_8H_6O_4$	0.0228324
$C_7H_{16}O$	0.000288427	$C_7H_{16}O$	0
$C_7H_{14}O_2$	0.000172029	$C_7H_{14}O_2$	3.912E-13
$C_7H_{10}O_2$	0.000192102	$C_7H_{10}O_2$	0
$C_7H_6O_3$	0.025528979	$C_7H_6O_3$	0.0182771
$C_7H_6O_2$	0.003088635	$C_7H_6O_2$	0.0166795
$C_6H_6O_2$	0.000168144	$C_6H_6O_2$	0.0114395
C_6H_6O	0.001702462	C_6H_6O	0.0003017
$C_5H_{10}O_2$	8.92682E-05	$C_5H_{10}O_2$	8.732E-07
$C_5H_{10}O$	0.000245629	$C_5H_{10}O$	0
$C_4H_6O_4$	0.012907614	$C_4H_6O_4$	0.0058132
$C_4H_4O_4$	0.048288508	$C_4H_4O_4$	0.0185457
$C_3H_4O_2$	0	$C_3H_4O_2$	0.0054044
CH_2O_2	0.046101874	CH_2O_2	0.0855379
Sulfur	0.010814077	Sulfur	0.0100308
Sodium	0.053955484	Sodium	0.0454526
CH_5N	0.000390006	CH_5N	0.0026723
KCl	0.004830431	KCl	0.0036704
Potassium	0.005034735	Potassium	0.0060875
Elemental Analysis		**Elemental Analysis**	
Carbon	32.57	Carbon	33.03
Hydrogen	2.93	Hydrogen	3.47
Nitrogen	0.07	Nitrogen	0.46
Oxygen	36.05	Oxygen	38.23
Sodium	20.52	Sodium	17.28
Potassium	2.88	Potassium	3.05
Sulfur	4.11	Sulfur	3.81
Other*	0.87	Other*	0.66
*Fed as Chlorine		*Fed as Chlorine	

Mass amounts for both the 100/0 and 85/15 simulation feeds added up to 0.263 grams, the average feed per minute for my 48 experiments. Equilibrium products were

also entered into the simulation. Note that any feed component could also exist as an equilibrium simulation product. Products not included in the feed are listed in the table below:

Table 11. Products of the simulation not included in feed.

Gas Components	Char Components
CO	Na_2CO_3
CH_4	Na_2S
methanol	Na_2SO_4
CH_2O	NaCl
ethane	K_2CO_3
propane	K_2S
H_2S	K_2SO_4
CS_2	ethyl MC or DMS
COS	methyl MC
n-propyl MC	dimethyl disulfide
isobutyl MC	ammonia
	H_2

Once all of the feed and product data were entered into the simulation, the software was instructed to iterate by temperature from 25 to 900°C at intervals of 20°C. The simulation then produced tabulated values versus temperature for the formation of H_2S, CO, CH_4, and H_2, theoretically the most important fuel gases produced in black liquor gasification. Tabulated values were entered into a spreadsheet and curves were generated for each 'mols produced versus temperature' relationship. Then, using equations from these curves and from the particle temperature versus time curves, and assuming a constant mass feed reacted per incremental time, a simulated molar amount produced per incremental time period for each species was able to be calculated. 0.0005 seconds was chosen as the incremental time. Therefore, after each 0.0005 seconds, a new molar amount for each species was calculated. The spreadsheet was extended down to a

residence time of 1.2 seconds, and the resulting mols produced for each species were summed. These molar amounts were then converted into mass amounts. Finally, fractions of feed elements (C, H, or S) recovered as a particular gas species (CH_4, CO, H_2, or H_2S) were calculated.

Assumptions not consistent with reality existed in this simulation. Because the HSC software was the only modeling software of ready disposal, the gasification process was modeled as an equilibrium process instead of a kinetic one. Therefore, no consideration of change in particle composition over time was taken into account. Essentially, at every time interval considered over the course of the reaction, the modeled particle composition was no different than the particle composition at time zero. Of course, the particle composition continually changed with time over the entire particle residence time in reality. Equilibrium modeling of a kinetic process attributed to the greatest error in the simulation results. As previously mentioned, it was assumed that a constant mass of feed was reacted per time over the entire 1.2-second residence time. In reality, rate of mass loss of the feed particles depended on the particles' changing composition and temperature over the entire residence time. This was an unavoidably bad assumption; it takes only about 0.03-0.04 seconds for complete loss of volatiles to occur in gasified black liquor particles of the size range considered at temperatures of 700 and 900°C (Sricharoenchaikul, 1994). Therefore, the chemical composition of the feed particles changed very rapidly after introduction into the reactor. Finally, the model takes into consideration no destruction of products once they are formed.

The equilibrium simulation did not account for any change in composition of feed particles or products over time. Because the rates of product gas formation and

destruction depended on the compositions and relative masses of the feed particles, smelt

products, and gas products at any particular time, the simulation results were in definite

error.
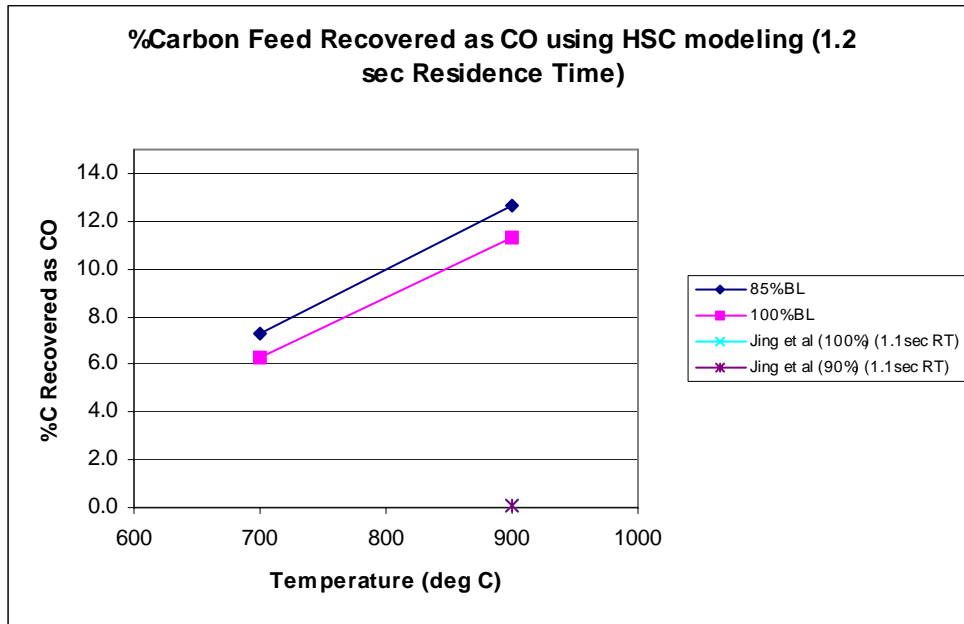
Figure 5. Effect of temperature on carbon recovery as CO for HSC simulation

I've included two data points from an unpublished paper (Jing, et al (1999)). Data from

this paper were useful because the LEFR experiments described in it also use the feed gas

composition of 70/15/15 nitrogen/carbon dioxide/water. In addition, the study examined

black liquor and secondary sludge feed solids mixtures. Specifically for the above graph,

the two points correspond to 100/0 and 90/10 liquor/sludge mixtures gasified for 1.1

seconds. It must be noted that the Jing, et al (1999) results for carbon recovery in the gas

phase were reported as percent recovery of *fixed* carbon fed as a particular carbon product

gas. It was assumed that the Jing, et al (1999) definition of fixed carbon fed was the

difference between the total carbon fed and the sum of total carbon volatilized and the

carbon ash (carbonate carbon) remaining in the char after the 1.1-second residence time

considered in the Jing, et al (1999) experiments. Jing, et al (1999) did not report mass of

liquor mixture fed, weight percent feed liquor recovered as char, weight percent of char

as carbon, or carbonate mass in char values for their experiments. Since these quantities

were required to convert fixed carbon into total carbon, like values from the experiments

described in this paper were used as estimates. The following equations describe how

percentages recovered as fixed carbon fed were transformed into percentages recovered

as total carbon fed:

fixed C in feed = feed C – volatilized C – ash C = (wt% C in feed)(wt fed) –   (26)
       ((wt% C in feed)(wt fed) -(wt% C in char/fume)(wt char/fume)) –
       (wt carbonate carbon in char/fume)

total C in feed = feed C   (27)

wt frac total C in feed as fixed C = (fixed C in feed) / (total C in feed)

%total C recovered as gas species x = (%fixed C recovered as gas species x) *   (28)
      (wt frac total C in feed as fixed C)

where: wt fed, wt% C in char, wt char, and wt carbonate C in char were estimated from like
      values obtained in Hammond's experiments; wt% C in feed and %fixed C recovered
      as gas species x values were supplied by Jing, et al (1999)

Because much of the data used to convert fixed carbon fed into total carbon fed had to be

assumed, some error in the resulting calculations existed. However, the approximations

used should have been close, and the associated error they produced should have been

relatively low. A larger source of error could be present if the Jing, et al (1999)

definition of fixed carbon differed from the one used in the above equations. Jing, et al

(1999) reported 0.5 and 0.46% recoveries of fixed carbon fed as CO at 900°C for the

90/10 and 100/0 liquor feeds, respectively. These values translated to 0.056 and 0.079%

recoveries as total carbon fed for the 90/10 and 100/0 liquor feeds. Notice that the

recovery for the 90/10 feed mixture was larger than the 100/0 recovery for percent fixed

carbon, and vice-versa for percent total carbon. This was because, from the results of the

experiments for this report, char recoveries tended to decrease as sludge addition to the

feed increased. This increased the percent of total carbon volatilized for the high sludge

feed additions versus the lower sludge feed additions. Although carbonate carbon

recoveries were higher for lower sludge feed additions, these differences were relatively

minor compared to the differences in char recovery. Therefore, fixed char recoveries

were lower for high sludge feed additions. Specifically, fixed carbon fed as a percentage

of total carbon fed was calculated as 11.2 and 17.1% for the 90/10 and 100/0 mixtures,

respectively.

As is obvious from the graph, the simulation recovery of feed carbon as CO is

much greater than the experimental results from Jing, et al (1999). Also, it appears that

the sludge mixture produced a bit more CO than black liquor alone in the simulation.

The opposite is true according to the Jing, et al (1999) results. Sricharoenchaikul, et al

(1994) experienced carbon recoveries as CO at levels of 1.1% for 700°C and 5.88% for

900°C for 1.5-second residence time using an all-nitrogen gas feed. These values are

closer in an absolute sense to the ones calculated in the simulation. The trending based

on temperature is also similar. However, because the Jing, et al (1999) values are so far

off from the simulation results, the conclusion must be made that the simulation results

contain large errors.

%Carbon Feed Recovered as CH$_4$ using HSC modeling (1.2 sec Residence Time)
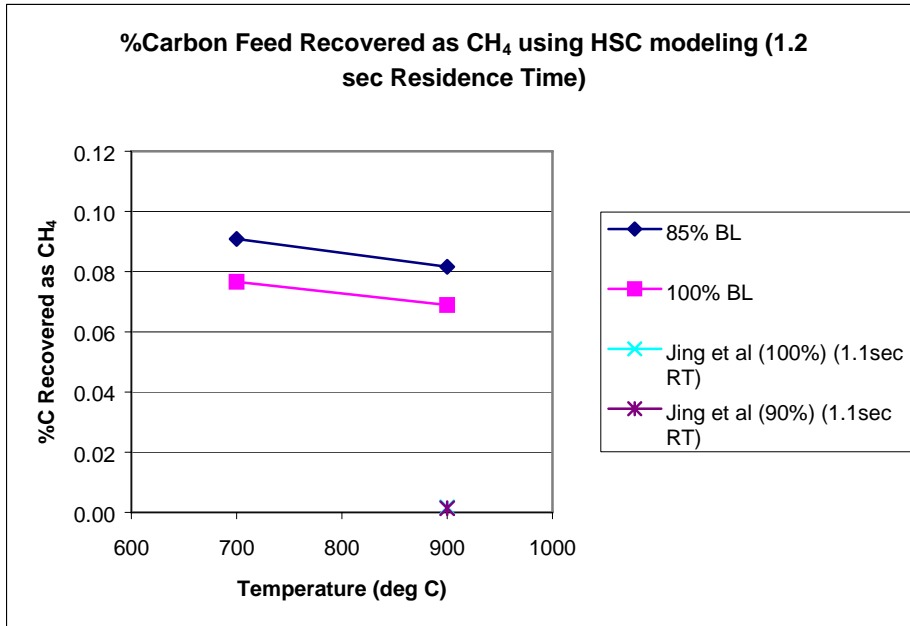
Figure 6. Effect of temperature on carbon recovery as CH$_4$ for HSC simulation

Jing, et al (1999) reported 0.024 and 0.022% recoveries of fixed carbon fed as CH$_4$ at 900°C for the 90/10 and 100/0 liquor feeds, respectively. These values translated to 0.0013 and 0.0017% recoveries as total carbon fed for the 90/10 and 100/0 liquor feeds. As was the case for CO, the simulation data show CO recovery much higher than that reported by Jing, et al (1999). Again, the simulation results differ from the results of Jing, et al (1999) in reference to which feed mixture produces more CH$_4$. Sricharoenchaikul, et al (1994) experienced 0.45% and 2.60% recoveries of feed carbon as CH$_4$ for temperatures of 700 and 900°C, respectively. Even though this data was obtained with an all-nitrogen gas feed, it casts doubt as to both the trending and absolute magnitude of the simulation values obtained for CH$_4$. Therefore, it must be concluded that the simulation results for CH$_4$ generation contain large errors.

%Sulfur Feed Recovered as H$_2$S using HSC modeling (1.2 sec Residence Time)
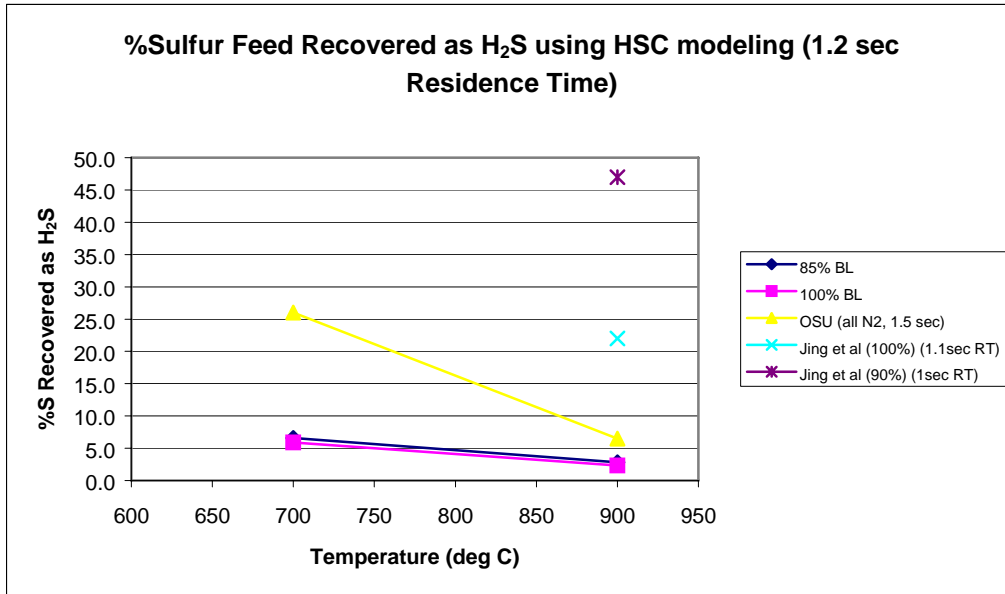
Figure 7. Effect of temperature on feed S recovery as H$_2$S for HSC simulation

Both the OSU (Sricharoenchaikul, et al (1994)) and the simulation data trend

downward in agreement with theory. The Jing, et al (1999) data shows a very large

difference between the H$_2$S generated from the sludge feed and the H$_2$S generated from

the black liquor feed at 900°C. This is in stark contrast to the difference observed

between the two simulation feeds. It must be concluded that the H$_2$S simulation data

contains large error and doesn't bolster the simulation results for either CO or CH$_4$

generation.

%Hydrogen Feed Recovered as H_2 using HSC modeling (1.2 sec Residence Time)
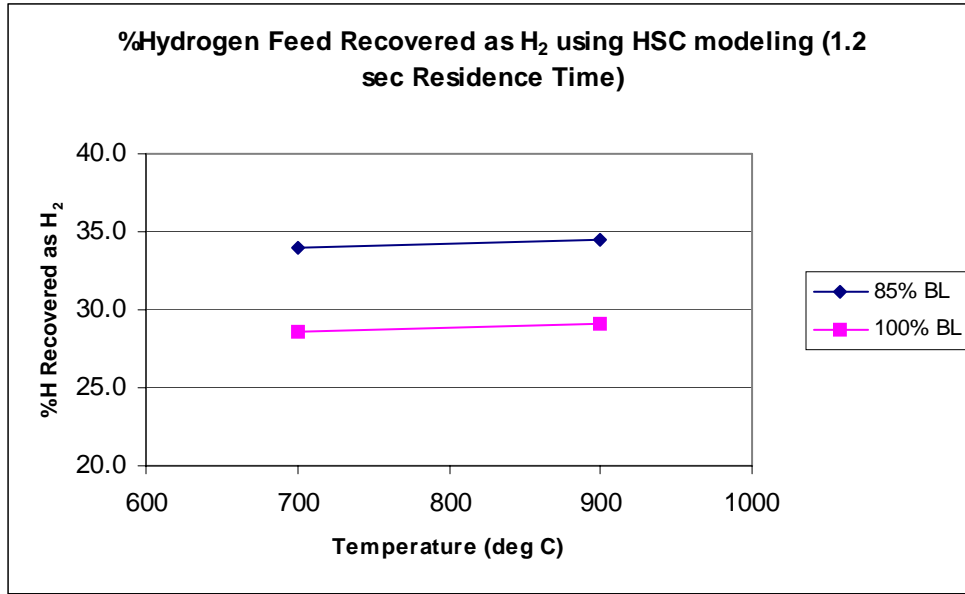
Figure 8. Effect of temperature on feed H recovery as H_2 for HSC simulation

There are no LEFR pilot data to which comparison of the simulation results for

hydrogen formation can be made. However, Whitty, et al (2001) reported that from

gasification pilot plant data, H_2 gas as a percentage of total dry product gas from an

oxygen-blown gasifier drops from about 33% to 25% from 900 to 1150°C. Although this

cannot be compared directly to the simulator percent recovery data, it does call into

question the positive trending observed in the simulation data. Therefore, there is no

evidence that supports the H_2 generation values obtained in the simulation. Considering

this and the results for the other product gas species studied in the simulation, accurate

heating values for product gases obtained in the experiments for which this report

describes could not be calculated. Therefore, Objective 1 was not accomplished.

Recovery of Organic Carbon in Char Samples

For the feed liquors and resulting chars obtained from the experiments discussed

in this report, it was assumed that total carbon contained in either feed or char equaled the

sum of the organic carbon and carbonate carbon contained in them. It was also assumed

that there was no carbonate carbon in the feed liquors. Percent of total feed carbon

converted to inorganic salt is a measure of the degree of gasification completion. A

greater carbonate carbon recovery in the product char per mass of carbon fed to the

reactor implies a greater degree of gasification completion. Since it was assumed that

organic carbon was the only other carbonaceous material in the char, degree of

gasification completion was assumed to decrease in proportion to increased recovery of

organic carbon in the char per mass total carbon fed to the reactor. The following

equations illustrate how percent recoveries of total carbon as organic carbon were

calculated:

wt frac Na_2CO_3 in char/fume sample = (Na_2CO_3 in vial) / (solution concentration) /   (29)
         (solution mass)

wt frac carbonate carbon in char/fume sample = (MW carbon) / (MW Na_2CO_3) *   (30)
         (wt frac Na_2CO_3 in char/fume sample)

carbonate carbon in char/fume sample = (wt frac carbonate) * (mass char)   (31)

wt organic carbon in char/fume sample = total carbon in char/fume -   (32)
         carbonate carbon in char/fume

% feed carbon recovered as organic carbon = (wt organic carbon) /   (33)
         ((wt frac carbon in feed) * (mass fed))

where: wt frac Na_2CO_3 in vial was obtained from GC reading

%Carbon Recovered as Organic Carbon vs. Temperature at Residence Time = 0.2 sec

%Carbon Recovered as Organic Carbon vs. Temperature at Residence Time = 0.7 sec

%Carbon Recovered as Organic Carbon vs. Temperature at Residence Time = 1.2 sec
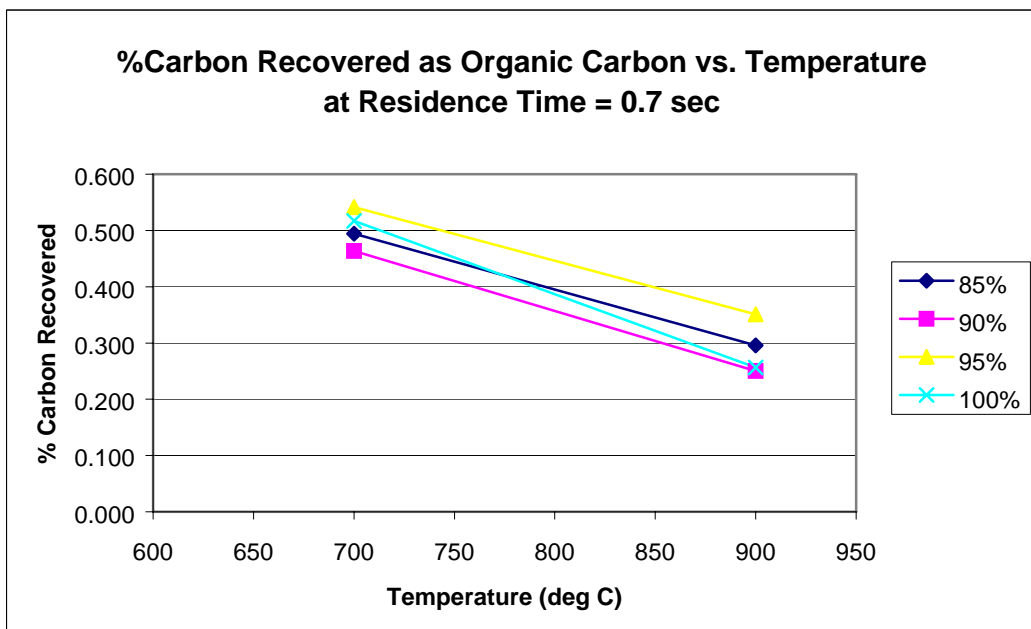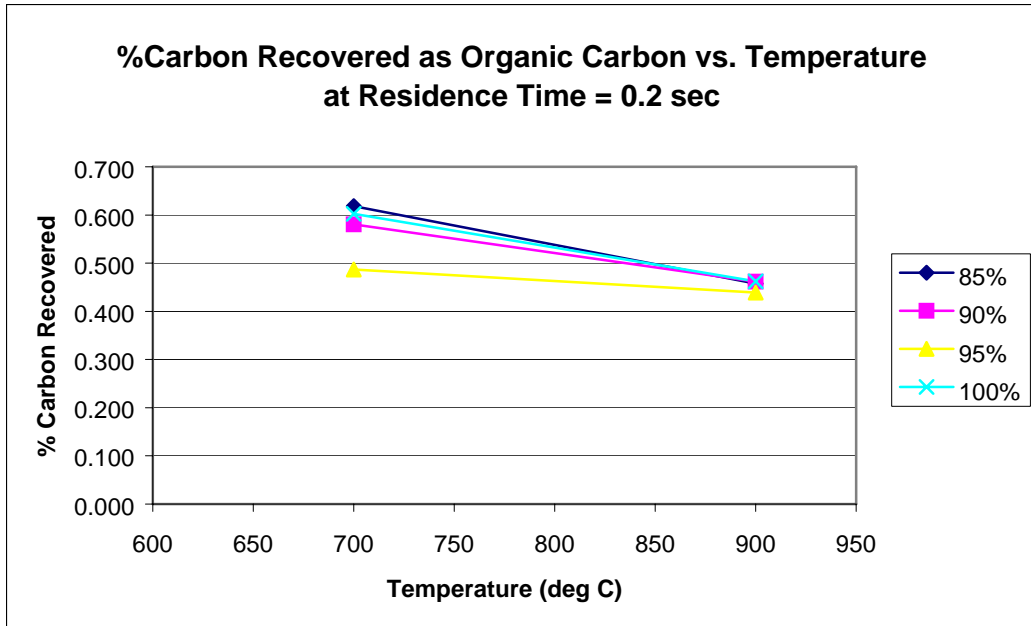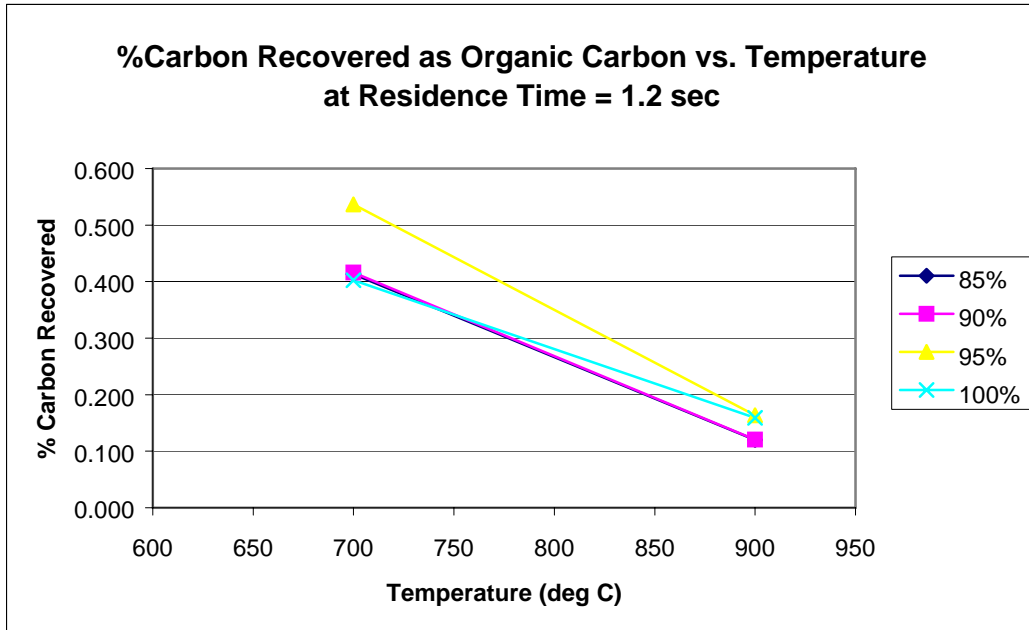
Figures 9, 10, 11. Effects of temperature on percent carbon recovered as organic carbon at RTs of 0.2, 0.7, 1.2 sec

All three above figures show a definite trending down of organic carbon recovery with increasing temperature. This was expected because feed decomposition rates tend to increase with increasing temperature. Also, the decrease in organic carbon recovery was more marked at higher residence times. No trending was observed in percent feed carbon recovery as organic carbon relative to percent sludge in the feed mixtures.
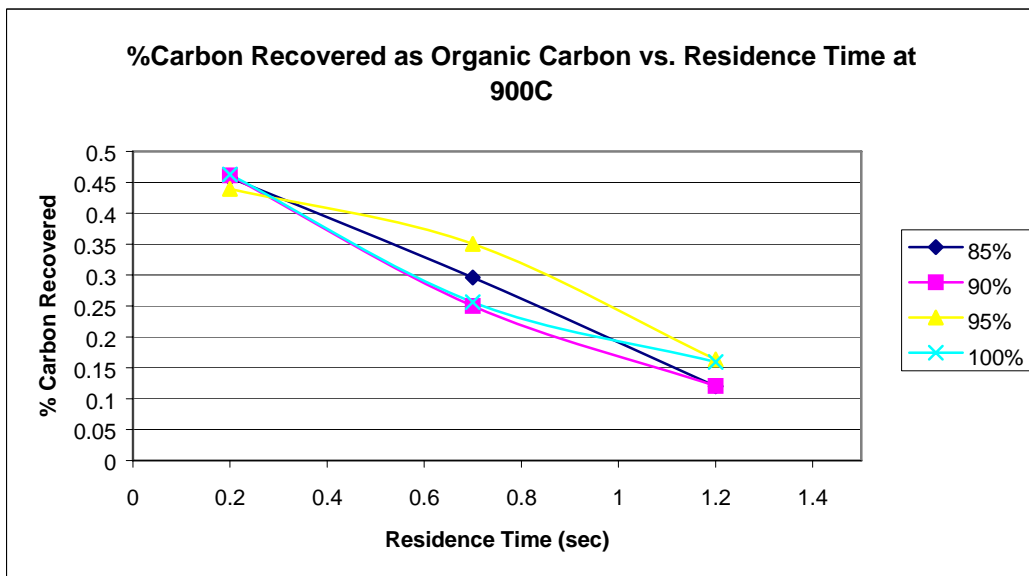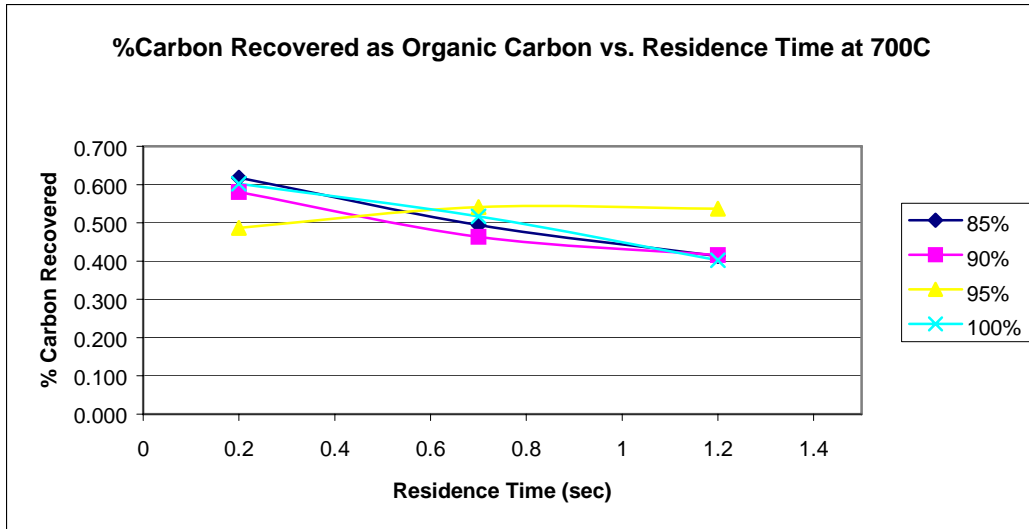
Figures 11, 12. Effects of residence time on percent carbon recovered as organic carbon at 700, 900°C

Figures 11 and 12 both show percent carbon recovery as organic carbon decreased

with residence time. This decrease, however, was much less rapid at 700°C than at

900°C. Therefore, rate of gasification was greater at 900°C (~30% decrease in total

carbon fed recovered as organic carbon after 1 second) than at 700°C (~10-15% decrease

in total carbon fed recovered as organic carbon after 1 second). Again, no concrete

correlation was made relative to gasification rate and sludge addition to feed. Therefore

it must be concluded that while an increase in temperature from 700 to 900°C accelerated

gasification rate, sludge addition to feed liquor up to 15% had no effect on gasification

rate.

Sulfur Components in Product Gases

      Although Objective 1 was not met, much data concerning sulfur gas species in

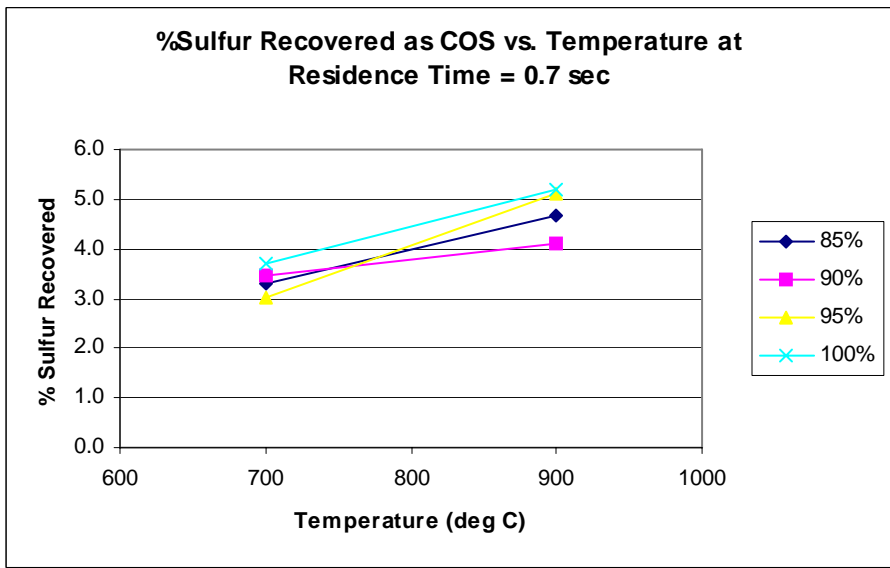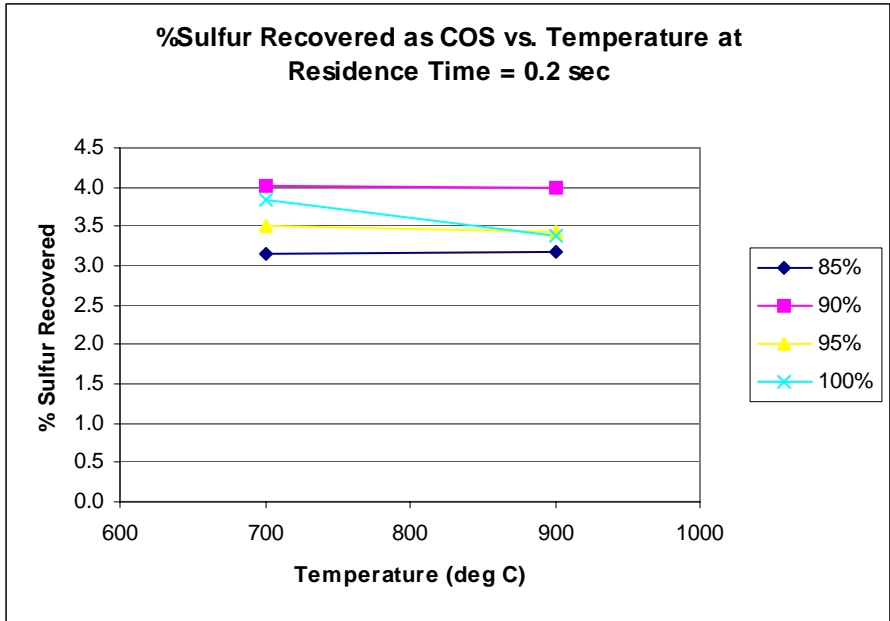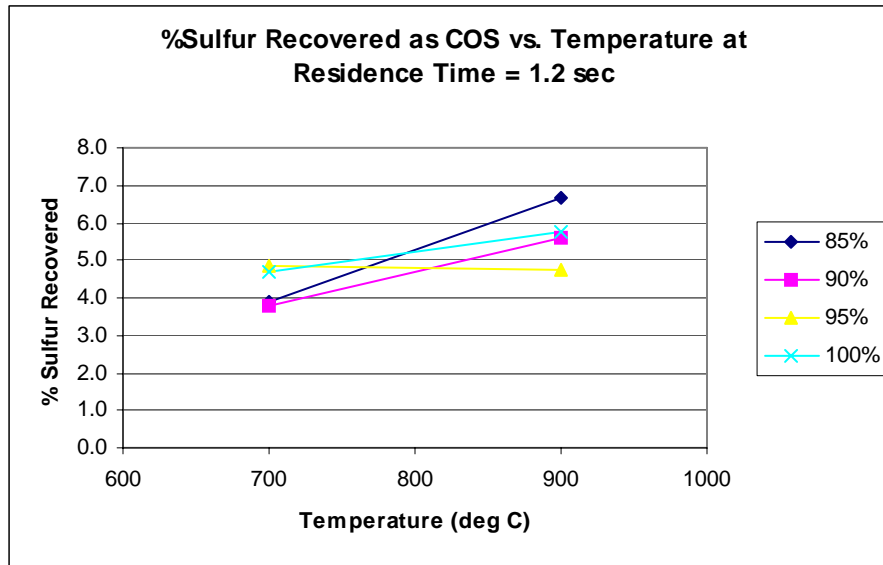gasification product gases were obtained. The results are discussed below:
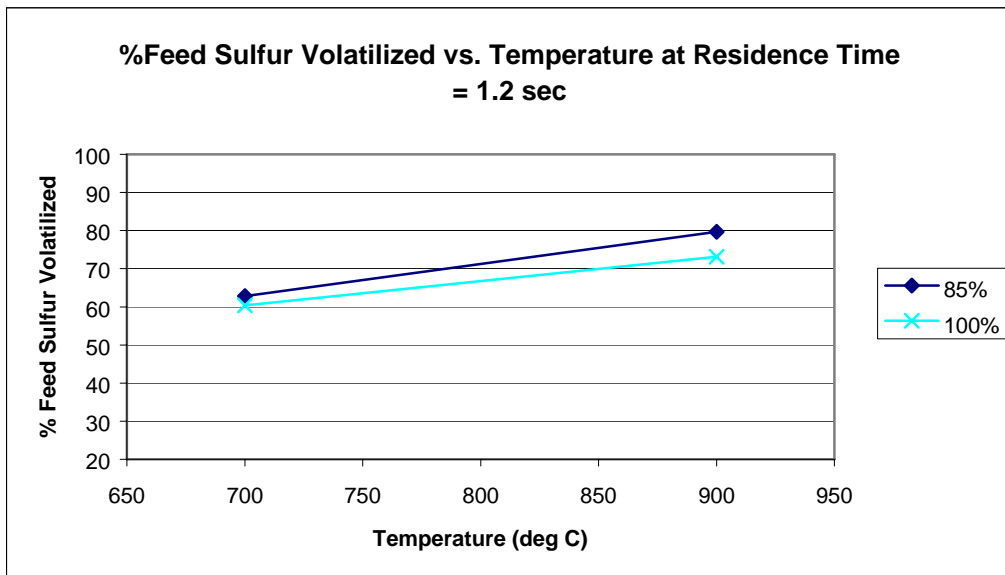
Figure 13. Effect of temperature on degree of sulfur volatilization

      The value of this relation is that it was derived from data obtained by metals

analysis rather than chromatographic analysis. Since the H_2S results from the

chromatograph were questionable, this relation gives some insight independent of an

overall sulfur recovery as indicated by chromatography. Percent feed sulfur volatilized

for both 100/0 and 85/15 sludge additions was about equal at ~63% at 700°C. However,

the 85/15 mixture was seen to volatize more readily with respect to sulfur than the 100/0

mixture at 900°C. Horenziak (1999) reported percent recovery of feed sulfur as gaseous

sulfur species at around 65% at 800°C and around 85% at 900°C for CO_2 gasification of

100% black liquor.

%Sulfur Recovered as COS vs. Temperature at Residence Time = 0.2 sec

%Sulfur Recovered as COS vs. Temperature at Residence Time = 0.7 sec

%Sulfur Recovered as COS vs. Temperature at
Residence Time = 1.2 sec

Figures 14, 15, 16. Effects of temperature on %feed sulfur recovered as COS at RTs of 0.2, 0.7,
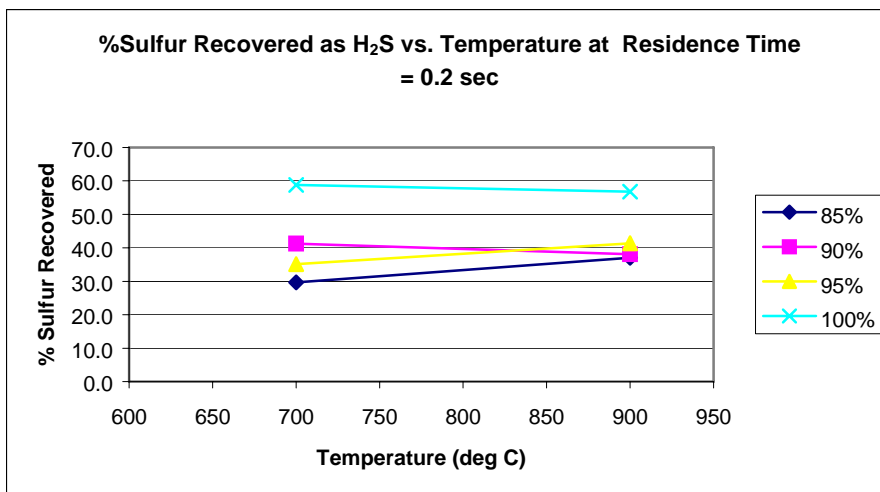1.2 sec

Percentage of feed sulfur recovered as COS was seen to increase about 1-3% from

700 to 900°C after 0.7 seconds of residence time. Relative to percentage of sludge

addition to feed, no significant trending was observed.
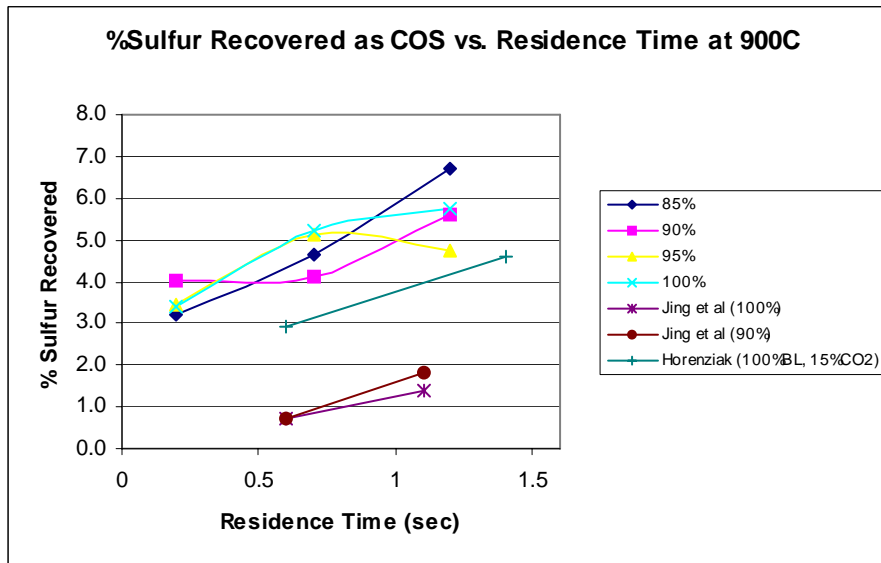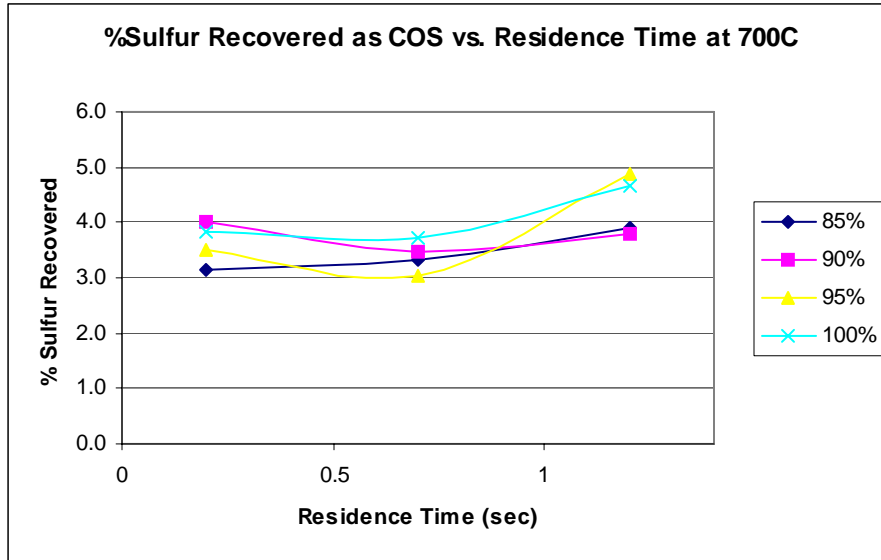
Figures 17, 18. Effects of residence time on %feed sulfur recovered as COS at 700, 900°C

At 700°C, recovery as COS was observed to stay relatively constant at around 3.5% up to

a residence time of 0.7 seconds. However, a slight increase of ~1-1.5% recovery was

observed from 0.7 to 1.2 seconds for the feed liquors with the lowest sludge

concentrations. At 900°C, no absolute recovery trending was seen relative to sludge

content in the feed liquor; however, it did appear that recoveries for the higher sludge

concentrations increased from 0.7 to 1.2 seconds, while the recoveries for the liquors at

lower concentrations seemed to level off. Although the experimental values differ in an

absolute sense from those reported by Jing, et al (1999) (experimental recoveries ~3

times higher), the more rapid rise in recovery for the sludge mixture than for the black

liquor feed after about 0.7 seconds was similarly noted by Jing, et al (1999). Horenziak

(1999) observed an increase in recovery with increased residence time similar to the

experimental results. Horenziak (1999) observed absolute recovery of COS at levels

much closer to the experimental results than did Jing, et al (1999). Sricharoenchaikul, et

al (1994) saw downward trending (29 to 8.5%) with a temperature increase from 700 to

900°C for an all-nitrogen secondary gas.

%Sulfur Recovered as H_2S vs. Temperature at Residence Time = 0.2 sec
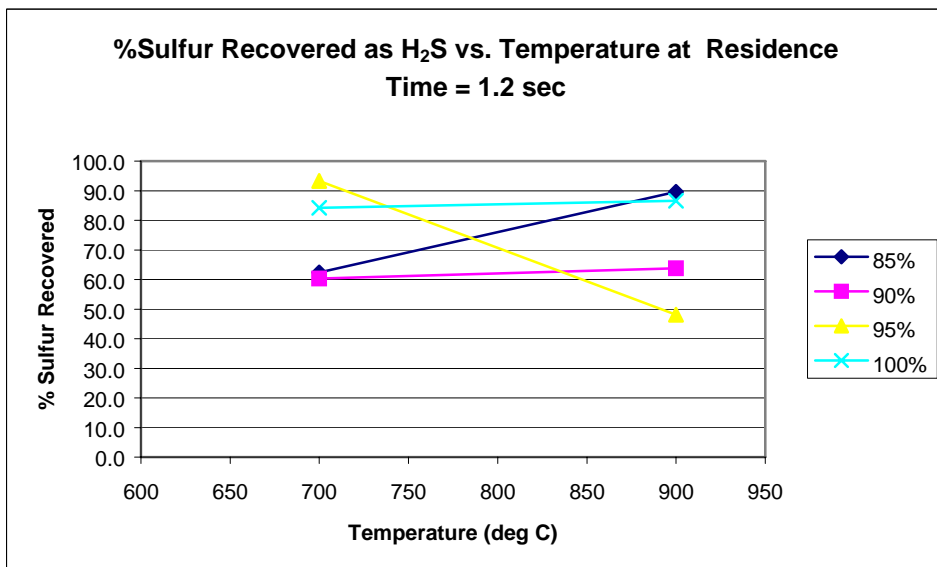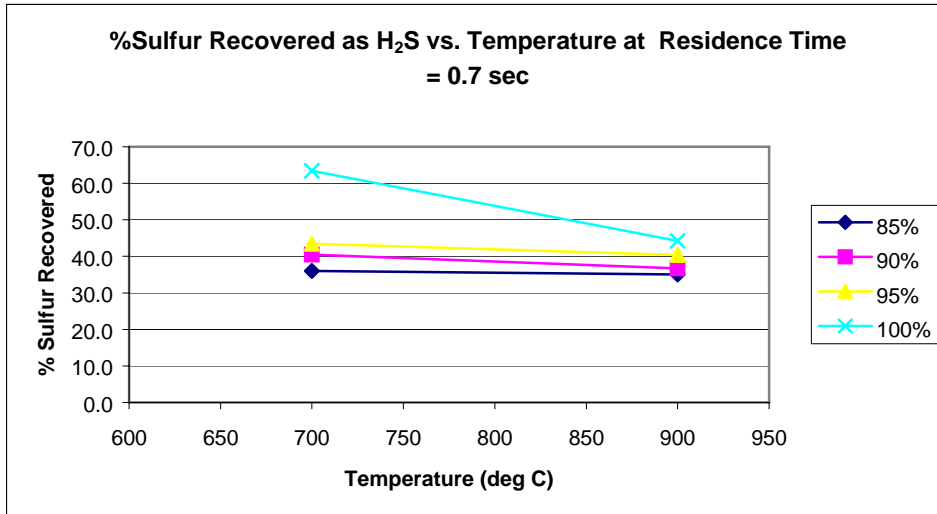
Figures 19, 20, 21. Effects of temperature on %feed sulfur recovered as H_2S at RTs of 0.2, 0.7,
                     1.2 sec

No trending was observed relative to temperature for H_2S recovery at 0.2 seconds.

A slightly negative trend (~2%) was observed at 0.7 seconds with respect to an increase

in temperature from 700 to 900°C for all but the 100/0 feed liquor. Percent recovery as

H_2S decreased ~15% for the 100/0 feed liquor at 0.7 seconds. At both the 0.2 and 0.7

residence times, a strong delineation existed between the different liquors. H_2S was

generated at lower quantities for the higher sludge addition liquors. At 1.2 seconds,

however, this delineation was lost, as was any temperature dependency.
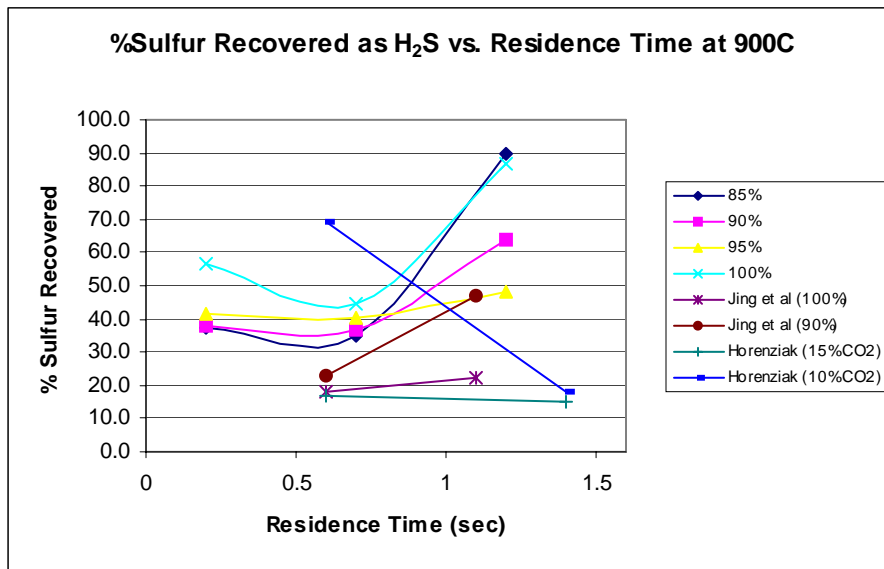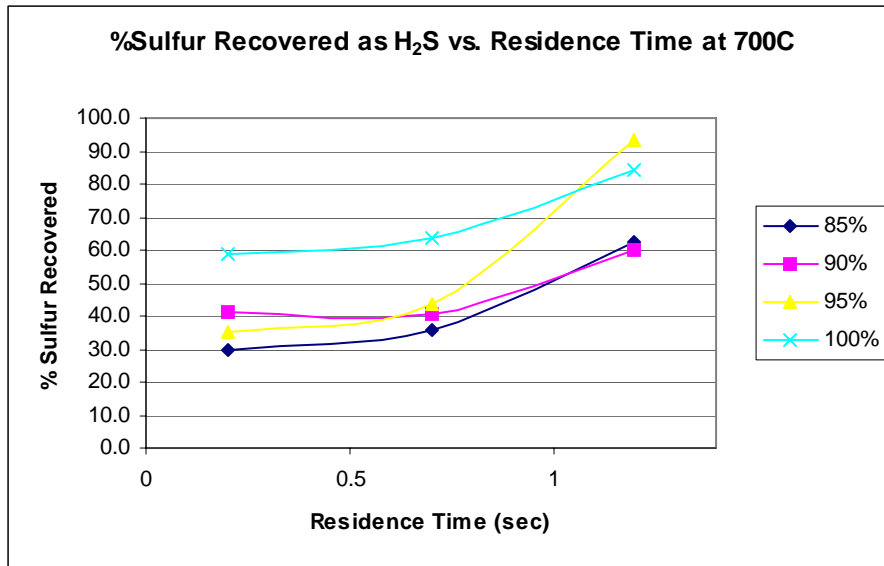
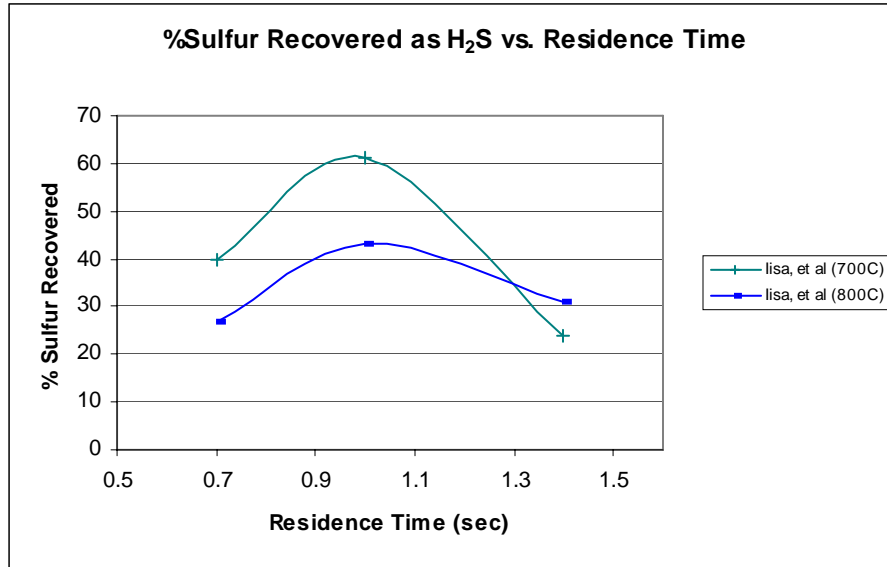Figures 22, 23. Effects of residence time on %feed sulfur recovered as H_2S at 700, 900°C
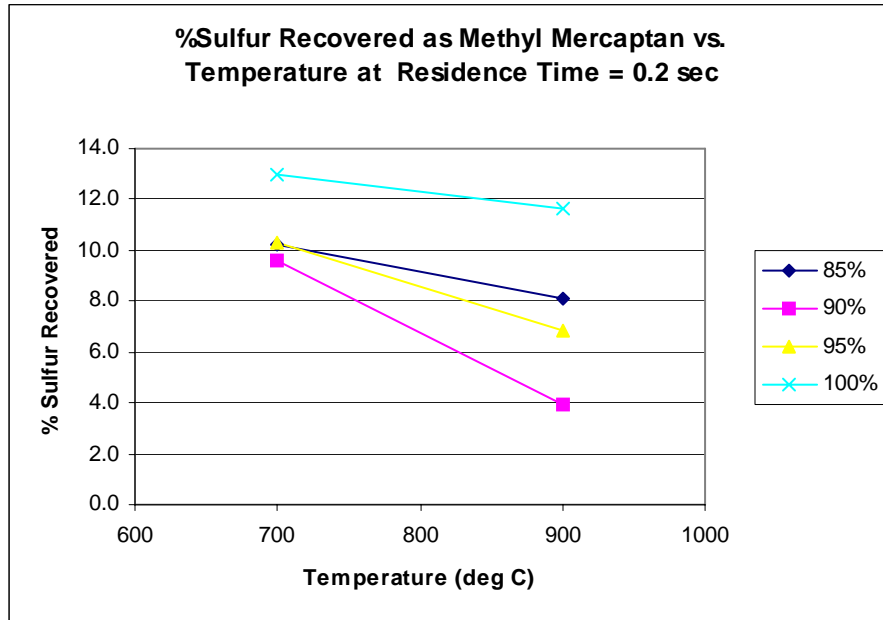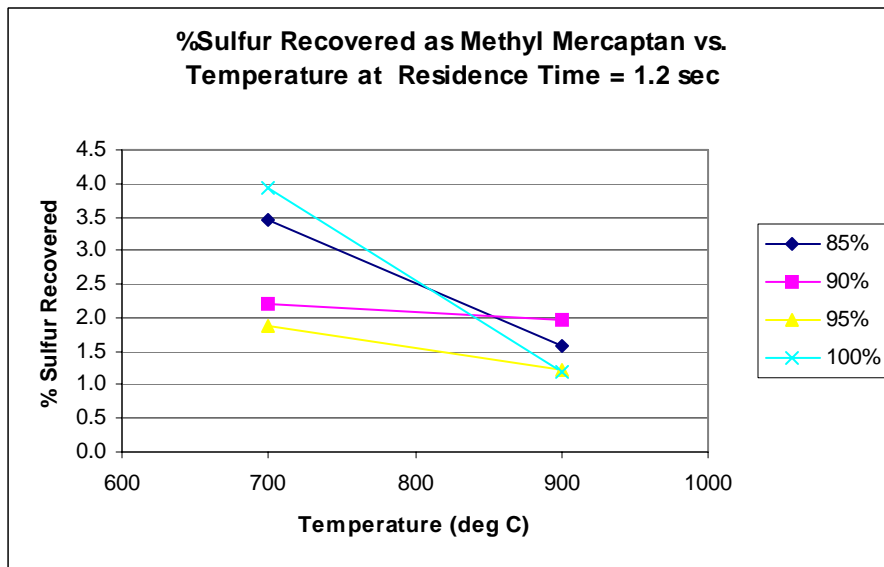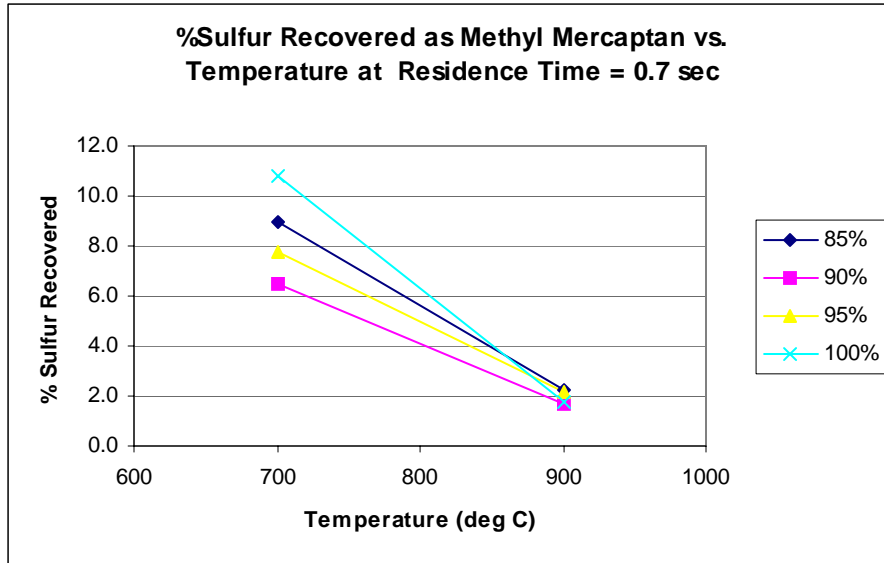
Figure 24. Effects of residence time on %feed sulfur recovered as H_2S at 700, 800°C (Iisa, 2001)

Figures 22 and 23 show that temperature had a relatively minor impact on H_2S generated.

Results from Whitty (2001) also showed a very slight dependence of H_2S generation on

temperature (~1% decrease from 900 to 1150°C). Figure 24, however, shows that Iisa, et

al (2001) reported a decrease of around 15% feed sulfur recovered as H_2S for a

temperature increase from 700 to 800°C for a secondary gas composition of 85/15

nitrogen/water vapor from 0.7 to 1.0 seconds. Horenziak (1999) reported an approximate

10% decrease in percent feed recovered as H_2S from 700 to 900°C at 1.4 seconds

residence time. Neglecting the sulfur recovery as H_2S for the 85/15 feed liquor at 900°C

and 1.2 seconds, the figures appear to indicate that lower sludge addition liquors tended

to produce less H_2S than did higher sludge addition liquors. The findings of Jing, et al

(1999) contradicted this, however. Theory states that H_2S concentration should decrease

upon increasing residence time. This was not observed experimentally at either

temperature, however. Results from Jing, et al (1999), also showed a trend against

theory. Horenziak (1999) reported trending with theory for a secondary gas composition

of 85/15 nitrogen/carbon dioxide. Iisa, et al (2001) reported that for 85/15 nitrogen/water

vapor steam gasification at 700°C, feed sulfur recovery as H_2S was around 40% at 0.7

seconds. It then rose to around 60% at 1.0 seconds and fell to around 30% after 1.4

seconds.

Experimental absolute recovery as H_2S ranged from about 30-90%. Iisa, et al

(2001) reported recoveries of 20-70% for steam gasification, while Horenziak (1999)

reported recovery of feed sulfur as H_2S from around 20–50% for various levels of CO_2

gasification.

%Sulfur Recovered as Methyl Mercaptan vs. Temperature at Residence Time = 0.7 sec

%Sulfur Recovered as Methyl Mercaptan vs. Temperature at Residence Time = 1.2 sec

Figures 25, 26, 27. Effects of temperature on %feed sulfur recovered as methyl mercaptan at
RTs of 0.2, 0.7, and 1.2 sec

Recovery of feed sulfur as methyl mercaptan showed an odd trend relative to

percent sludge addition in feed liquor. The 100/0 liquor showed the most recovery as

methyl mercaptan, while the 85/15 liquor showed the second-most. Conclusions

regarding recovery as methyl mercaptan versus temperature were not made,

consequently. There was a definite downtrend of recovery as methyl mercaptan versus

temperature for all residence times, with the most marked being at 0.7 seconds (~6%

decrease from 700 to 900°C).
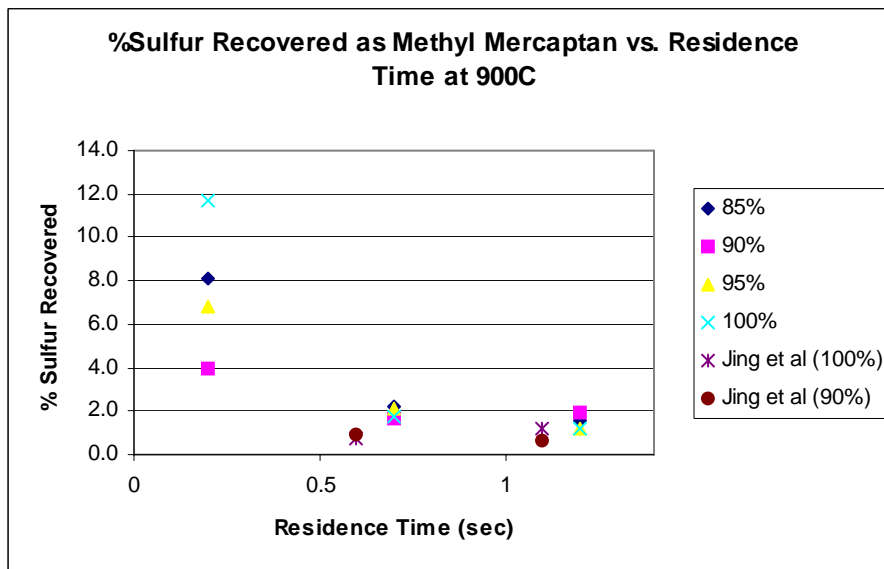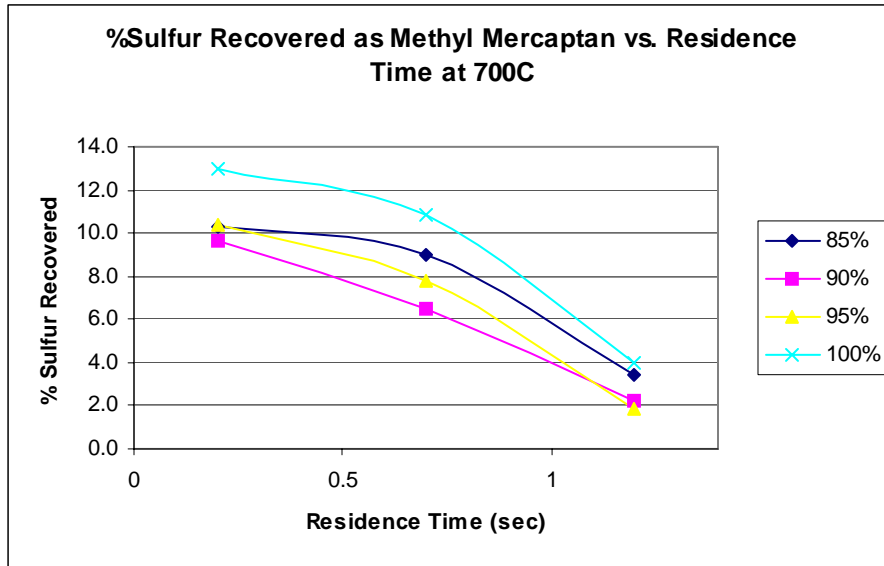
Figures 28, 29. Effects of residence time on %feed sulfur recovered as methyl mercaptan at 700, 900°C

Experimental data for methyl mercaptan generation very closely resembled both the Jing,

et al (1999) data and the steam gasification data from Horenziak (1999). Figure 29 shows

no trending in the Jing, et al (1999) data with respect to feed liquor composition.

Horenziak observed methyl mercaptan recoveries falling from about 3.5 to 1.5% upon a

temperature increase from 700 to 900°C for a 90/10 nitrogen/water vapor secondary gas

at 1.4 seconds residence time. Upon various levels of CO_2 gasification at various levels,

however, Horenziak observed hardly any methyl mercaptan generation. Only around

0.2% recovery was observed at 1.4 seconds residence time. This suggested that methyl

mercaptan is only generated at significant quantities by steam gasification, and not by

CO_2 gasification. Experimental data showed that at 700°C, there existed a fairly linear

decrease of methyl mercaptan recovery (~10.5 to 3%) for a residence time increase of 0.2

to 1.2 seconds. At 900°C, experimental data showed a recovery decrease from about 8 to

2 to 1.5% for residence time increases from 0.2 to 0.7 to 1.2 seconds.

%Sulfur Recovered as n-propyl Mercaptan vs. Temperature at Residence Time = 0.2 sec

%Sulfur Recovered as n-propyl Mercaptan vs. Temperature at Residence Time = 0.7 sec

%Sulfur Recovered as n-propyl Mercaptan vs. Temperature at Residence Time = 1.2 sec
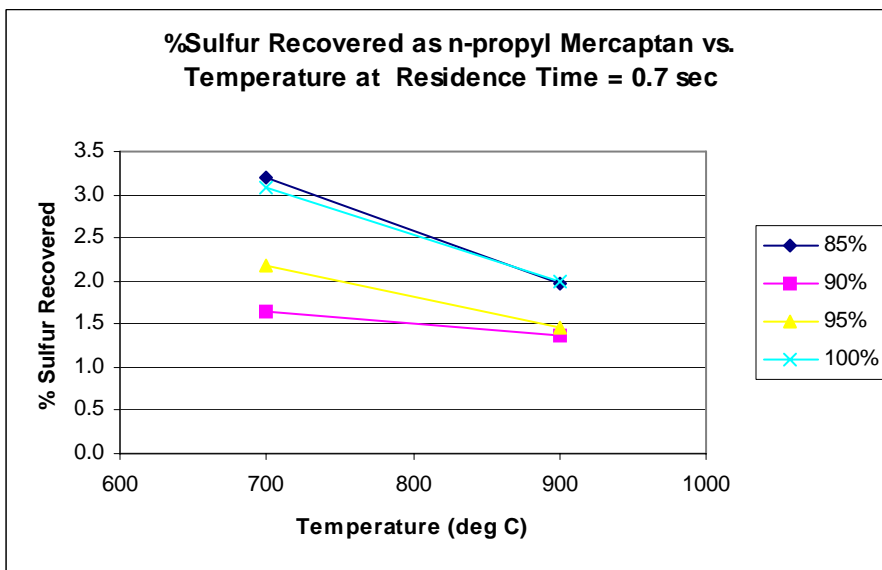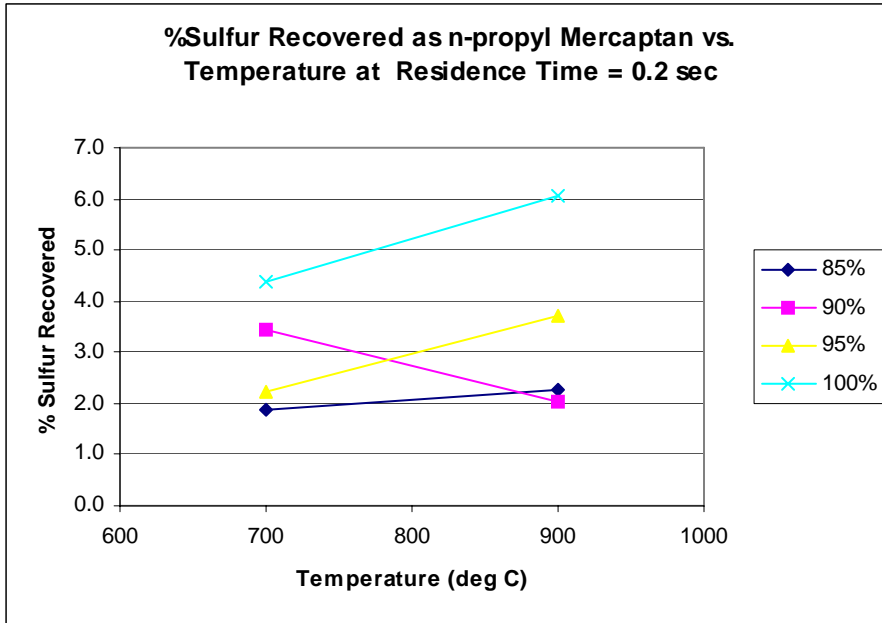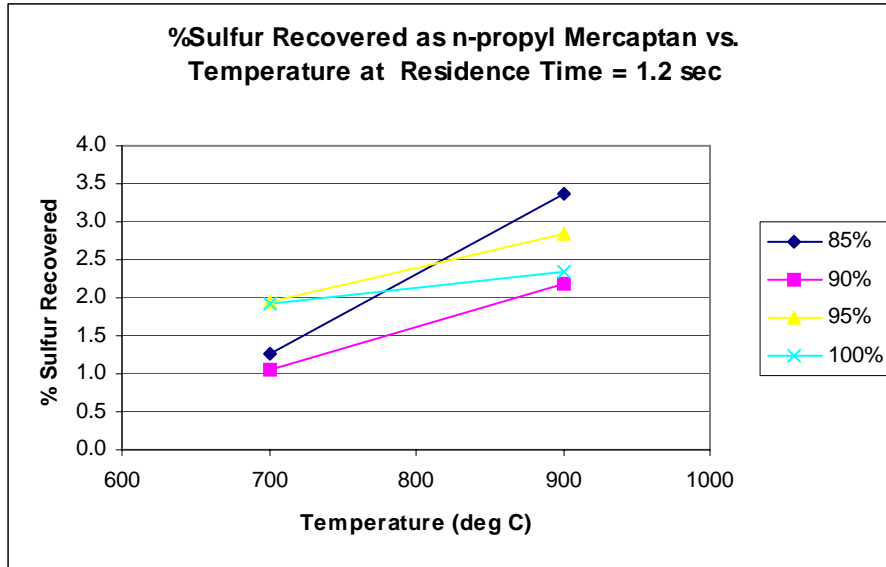
Figures 30, 31, 32. Effects of temperature on %feed sulfur recovered as n-propyl mercaptan at
RTs of 0.2, 0.7, and 1.2 sec

No trending was observed for either temperature or liquor composition dependence at 0.2 seconds residence time. At 0.7 seconds, percent recovery of feed sulfur as n-propyl mercaptan decreased from ~2.5 to 1.75% upon a temperature increase from 700 to 900°C. At 1.2 seconds, percent recovery increased from ~1.5 to 2.5% upon a temperature increase from 700 to 900°C. No observable trending was present regarding liquor composition.
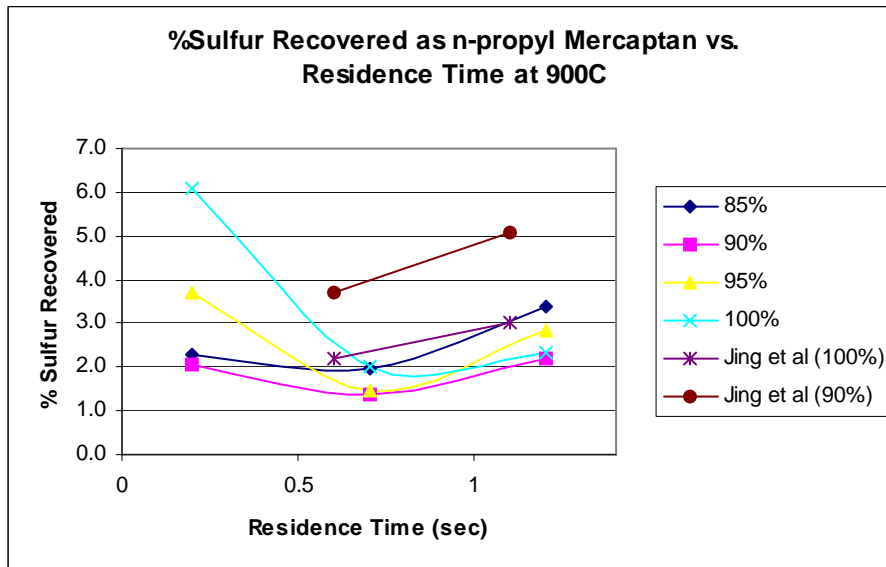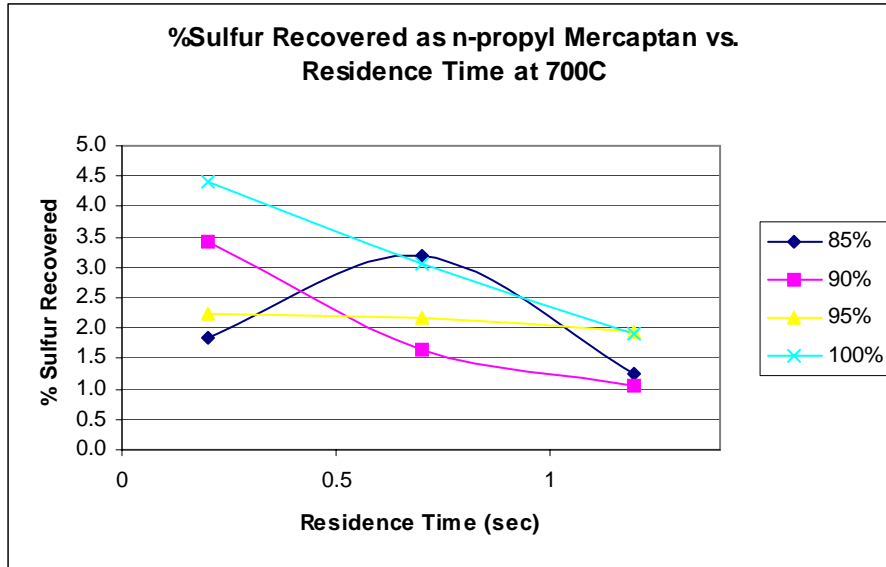
Figures 33, 34. Effects of residence time on %feed sulfur recovered as methyl mercaptan at 700, 900°C

Horenziak (1999) observed a slight decrease in recovery at 900°C for feed sulfur

recovery as n-propyl mercaptan versus residence time for CO_2 gasification from 10-20%

CO_2 in secondary gas. Horenziak also observed a drop from about 5 to 3% recovered

with a residence time increase from 0.7 to 1.2 seconds. Although the trending is

relatively the same, Horenziak observed an increase in recovery from about 1 to 3% upon

a temperature increase from 700 to 900°C for various levels of CO_2 gasification at 1.4

seconds residence time. Data from Jing, et al (1999) agreed with the experimental data,

except that about a 1.5-2% recovery increase existed for the 90/10 sludge mixture.

NOx Precursor Formation

Budget and time constraints did not allow for feed liquor samples to be analyzed

for total nitrogen content. Therefore, nitrogen contents in feed liquors were assumed

based on the Schwanz (1999) elemental analyses previously mentioned. Since

Schwanz's sludge source was identical to the one used for the experiments described in

this report, the assumed nitrogen contents for the liquors were probably relatively

accurate. As previously mentioned, the NOx meter used in the experiments only

measured ammonia nitrogen after it had been converted to NO. Concentrations of

ammonia in the product gas were calculated as follows:

ppm NH3 in product gas = (NOx meter ppm output) /   (34)
$\qquad$ (0.45 for 700°C or 0.60 for 900°C)

%Nitrogen Recovered as Ammonia vs. Temperature at Residence Time = 0.2 sec

%Nitrogen Recovered as Ammonia vs. Temperature at Residence Time = 0.7 sec
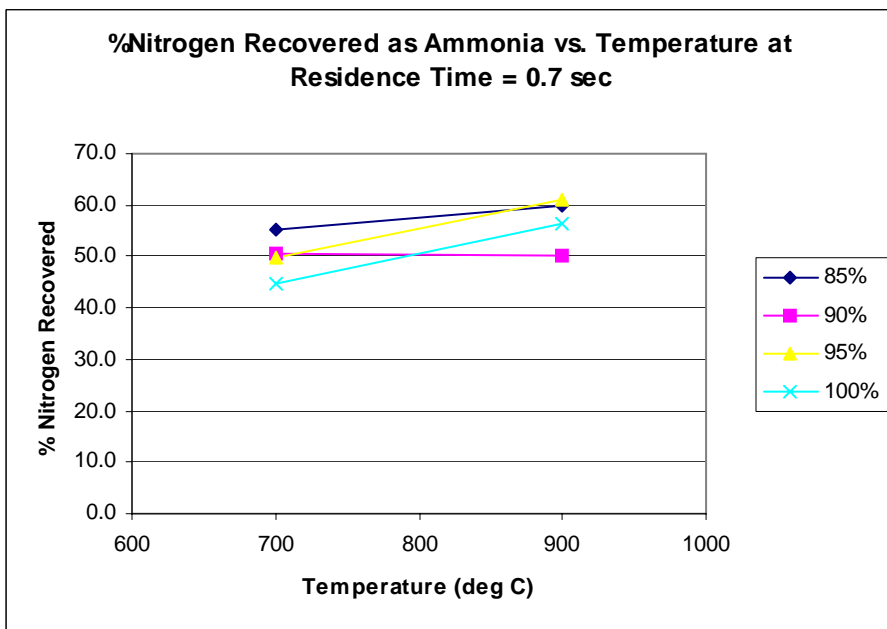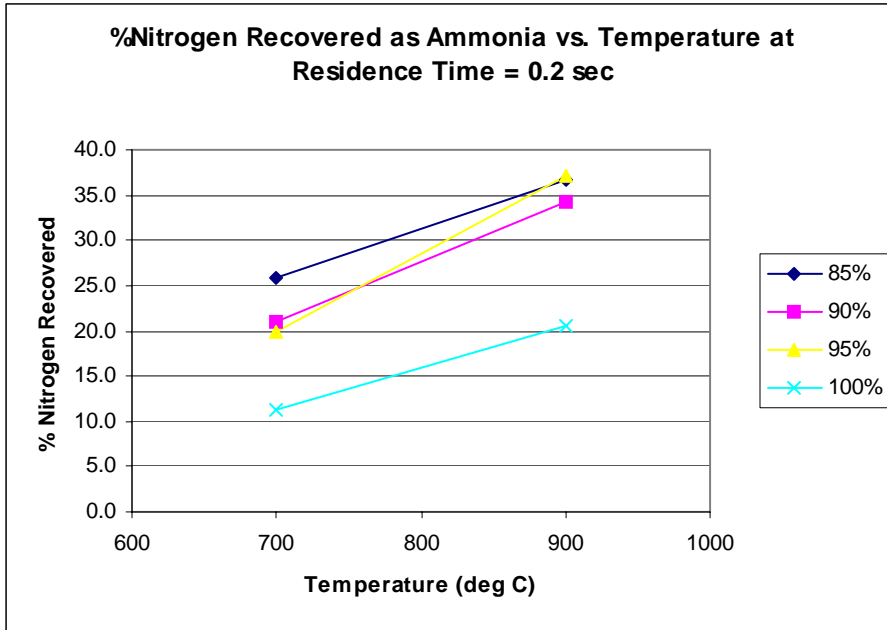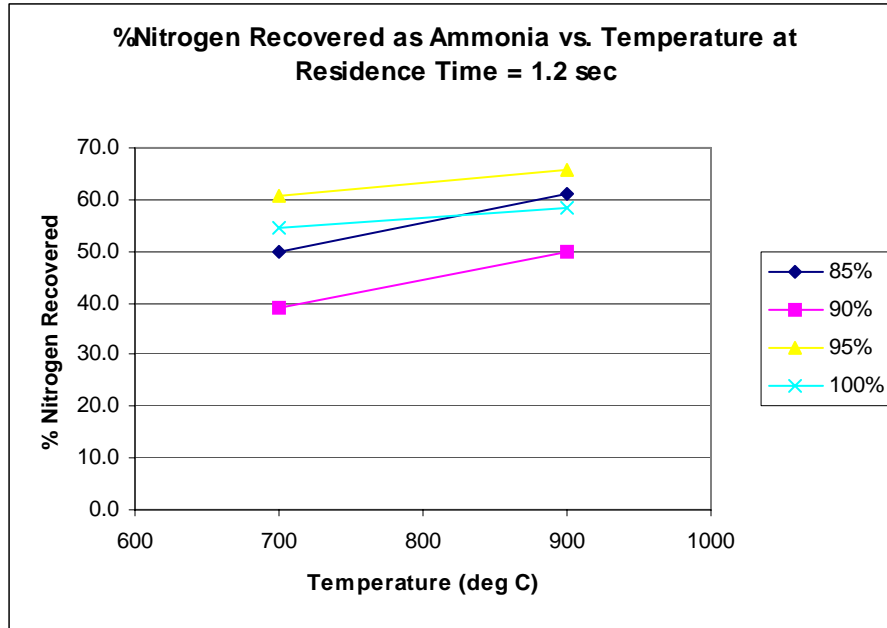
Figures 35, 36, 37. Effects of temperature on %feed nitrogen recovered as ammonia at
RTs of 0.2, 0.7, and 1.2 sec

Recovery of feed nitrogen as ammonia increased about 10% with temperature increases from 700 to 900°C for both 0.7 and 1.2-second residence times. 0.2 seconds showed slightly greater temperature dependence, increasing around 15% feed nitrogen recovered from 700 to 900°C. 0.2 seconds also showed the smallest generation of ammonia at around 23 to 35% feed nitrogen recovered as ammonia. Generation at 0.7 and 1.2 seconds remained at a steady 50 to 60% feed nitrogen recovered as ammonia.
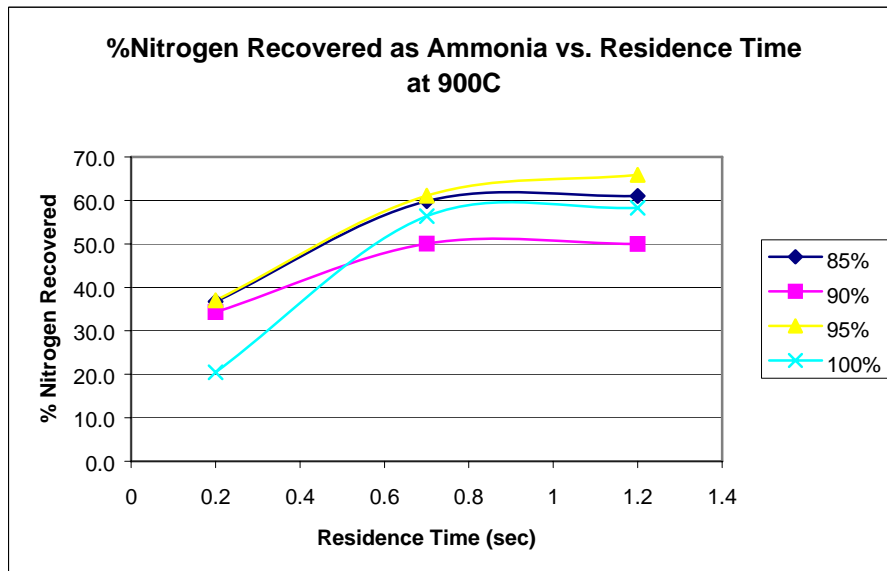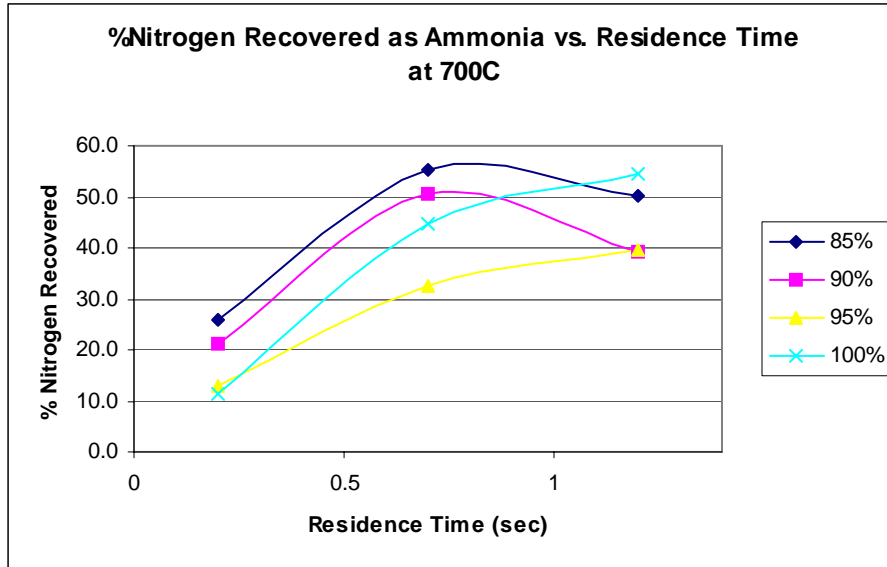
Figures 38, 39. Effects of residence time on %feed nitrogen recovered as ammonia at 700, 900°C

Figures 38 and 39 show that ammonia generation increased until about 0.7 seconds and

then leveled off. Sricharoenchaikul, et al (1994) reported that after 0.5 seconds, the

fraction of feed nitrogen remaining unvolatilized stayed constant at around 50% at

900°C. Apparently, almost all of the volatile nitrogen transferred to the gas phase

relatively quickly upon entering the reactor. Experimental results seemed to follow this

theory. Percent feed nitrogen recovered seemed relatively independent of feed liquor

composition, except in the case of the 0.2-second residence time. The 85/15 feed mixture

evolved more nitrogen as a percentage of feed nitrogen than did the 100/0 mixture. It

should be noted that, from a strict ppm output sense, the 85/15 liquor mixture, on

average, produced a ppm reading about 4-5 times that of the 100/0 liquor feed.

Therefore, even though percent nitrogen recovered as NOx was not notably dependent on

liquor composition, actual output of NOx was much higher for the higher sludge addition

liquors.

Metals Recovery

Non-process metals (NPMs) are undesirable in the Kraft recovery cycle. Many

negative factors arise from high levels of NPMs. Dregs carryover can result in calcium

carryover in the white liquor, decreased lime mud settling rate in the white liquor

clarifier, decreased lime mud washing efficiency, poor weak-wash clarity, increased TRS

lime kiln emissions, and increased fuel requirements in the lime cycle.
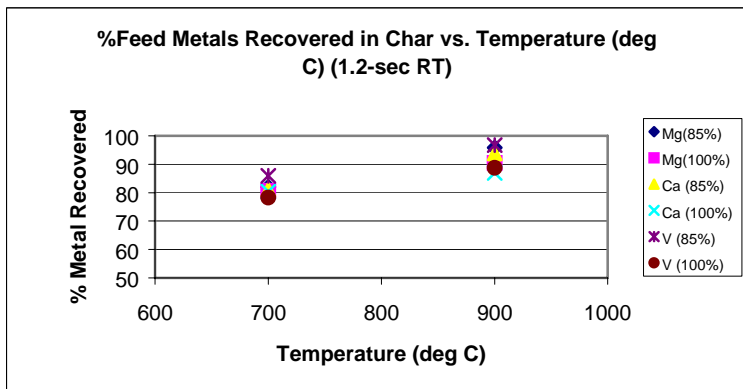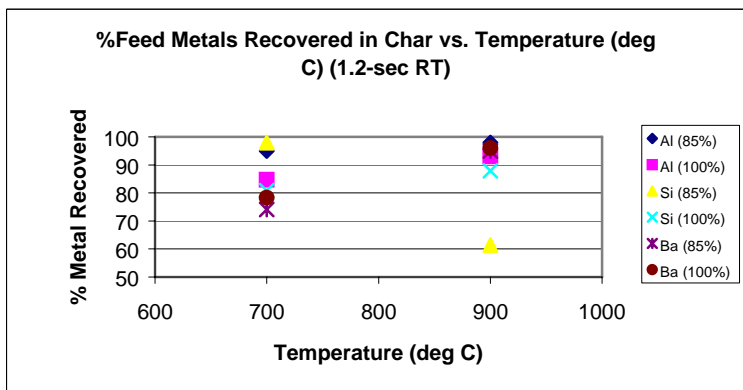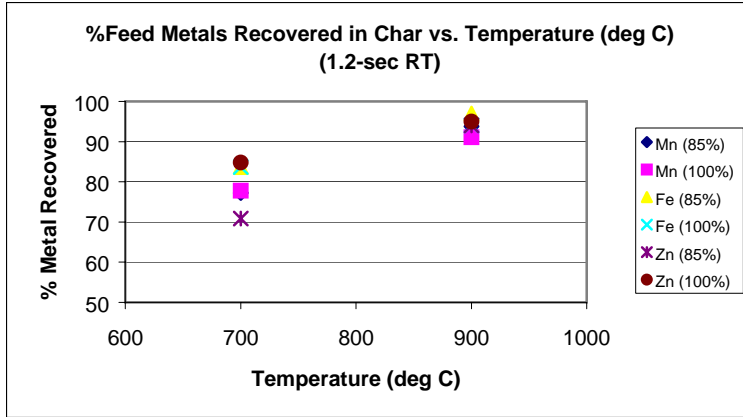
Figures 40, 41, 42. Effects of temperature on percent metals fed recovered in char

Figure 40 shows that zinc recovery at 700°C was about 15% less for the 85/15 feed liquor than for the 100/0 feed liquor. Barium showed the same trend. However, aluminum and silica showed that recoveries at 700°C were about 15% higher for 85/15 feed as opposed to the 100/0 liquor. The only metal that significantly opposed the trend

of an approximate 10% gain in recovery percentage upon temperature increase from 700

to 900°C is silica. Since recovery of silica drops over 30% at 900°C, the result is

probably not feasible and probably contains a large error. Therefore, conclusions were

not drawn from it. Vanadium, a corrosive, seemed to be recovered in greater abundance

for the 85/15 mixture than for the 100/0 mixture (by ~7-8%) for both temperatures.

Magnesium forms an oxide that inhibits the slaking rate of CaO. Magnesium was

recovered in the 85/15 product char in about 6% greater abundance than in the 100/0 char

at 900°C. Calcium recovery at 900°C was very similar to that of magnesium. As a rule,

percent recoveries at 700°C averaged in approximately the low 80s. They averaged in

the mid 90s at 900°C. In theory, a greater percentage of metals fed should be volatilized

at the higher temperature. This was not observed in this study. Perhaps a portion of the

volatilized metals condensed on the walls of the quench tube before they entered the

collection cyclone. However, this still does not account for there being a larger

percentage of metals recovered at 900°C than at 700°C in the char. From the

experimental data, it can be concluded that gasification at 900°C will lead to a higher

concentration of green liquor NPMs than gasification at 700°C. However, theory states

otherwise. The 85/15 feed mixture seemed to retain the more undesirable NPMs (Mg, V,

and Al) in higher abundance than did the 100/0 feed liquor at 900°C.

Conclusions

Objective 1, calculating heating values for the different sludge/liquor feed

mixtures was not accomplished. H_2, CO, and CH_4 were not detectable with the gas

chromatograph used in the experimentation, and attempts to simulate generation of these

compounds proved unsuccessful. The assumptions that had to be made (equilibrium

process, mass of particles reacted constant over time, no destruction of product gases once formed) may have caused the simulation data to contain large error. Transforming the Jing, et al (1999) data from fixed carbon input to total carbon input may also have introduced error. No reasonable conclusions could be drawn from the simulation data.

Percent of total carbon recovered as organic carbon in the product char decreased with temperature and residence time. Therefore, rate of gasification is greater at 900°C (~30% decrease in total carbon fed recovered as organic carbon after 1 second) than at 700°C (~10-15% decrease in total carbon fed recovered as organic carbon after 1 second). No concrete correlation was made between gasification rate and sludge addition to feed. The 85/15 mixture was seen to volatize more readily with respect to sulfur than the 100/0 mixture at 900°C.

H_2S, COS, methyl mercaptan, and n-propyl mercaptan were the major sulfur species identified from the gasification experiments. Ethyl mercaptan, isobutyl mercaptan and carbon disulfide did not appear to be formed in any significant extent during gasification between 700 and 900°C. The following conclusions were drawn concerning individual sulfur gas species:

1. **COS:** Relative to percentage of sludge addition to feed, no significant trending was observed. Trending generally agreed with past experiments at 900°C; however, absolute recoveries for COS were higher than those observed in past studies. Therefore, absolute recoveries of COS observed in this study are questionable.

2. **Hydrogen sulfide:** H_2S was generated at lower quantities for the higher sludge addition liquors. At 1.2 seconds, however, this delineation was lost.

Temperature had relatively minor impact on H_2S generated, which goes against theory. Therefore, although upward trending in H_2S recovery was observed from 0.7 to 1.2 seconds in the Jing, et al experiments, the absolute recoveries of H_2S observed are questionable, as are the trends observed.

3. **Methyl Mercaptan:** No concrete trending regarding recovery as methyl mercaptan versus temperature was observed, although the 100/0 feed stock produced more methyl mercaptan as a percentage of sulfur fed than did the other feed liquors. Trending and absolute generation of methyl mercaptan correlated well with past experiments.

4. **n-Propyl Mercaptan:** Other than at 900°C and 0.2-seconds residence time, no observable trending was present regarding liquor composition. While trending agreed with the Jing, et al results at 900°C, the Jing study showed an increase in n-propyl mercaptan recovered with increased secondary sludge addition. This calls into question the experimental results.

No correlation between ammonia recovery and sludge addition was observed. However, the concentration of ammonia produced by the 85/15 feed stock was about 4-5 times higher than that produced by the 100/0 feed stock. Therefore, adding secondary sludge to a recovery process will produce more ammonia upon incineration than will incineration of black liquor alone. Absolute recoveries correlated well with the results obtained by Sricharoenchaikul, et al. Therefore, they are concluded to be correct.

Results of the metals recovery at the two experimental temperatures are inconclusive. All experimental data showed that recovery increased from 700°C to 900°C. However, since the findings go against theory, no conclusions can be made other

than experimental error in either producing or testing the char samples. The 85/15 feed

mixture seemed to retain the more undesirable NPMs (V, and Al) in higher abundance

than did the 100/0 feed liquor at 900°C. This may be a consideration against adding

sludge to the recovery process.

Recommendations/Guidelines for Future Work

Since this report failed to evaluate the heating value differences between various

secondary sludge/black liquor feed mixture product gases, gathering data pertinent to this

subject may be of interest. Future researchers may consider the following:

1. Perform analyses of product gas samples from gasification of various compounds
   with cryogenic gas chromatography. If excellent separation of fuel gases is not
   obtained, then consider purchasing a 60-meter column to facilitate longer, more
   distinctly separate residence times. The current HP 5890 Series II GC designated
   for LEFR use is capable of cryogenic operation. A liquid nitrogen dewar adapter
   attachment is all that is required.

2. Perform substantial research concerning optimal oven programs and other
   chromatograph specs to ensure precise results. Seek out the Agilent
   professionals; they have much information at their disposal.

3. To save budget money and calibration time, purchase calibration gases in large
   quantity mixtures. Be sure to use calibration gases that are not more than a year
   old.

4. To obtain accurately representative gas samples, variations in the feed rate of
   solids to the LEFR must be either avoided or rendered insignificant. Adhering to
   a strict cleaning schedule of the LEFR feed tubing and injector is the best way to

ensure a constant flow of solids during an experiment. The feed tubing should be blown out with nitrogen and the injector should be thoroughly brushed out immediately following completion of an experiment. Any water vapor flowing into the LEFR during an experiment should be shut off when experimentation is complete. Feed tubing should be switched out and cleaned with methanol after every other experiment. Ideally, no more than four experiments should be performed in a single day. This will prevent build-up of char particles at the top of the ceramic collector. Ideally, a maximum of four experiments should be run before the reactor is cooled and the collector is manually cleaned and realigned. Proper collector alignment is crucial for complete char recovery, as is laminar, centered flow of the feed solids. The ceramic flow straightener must be perfectly intact to ensure laminar particle feed. One must not be overzealous when cleaning the injector if it becomes plugged, lest the risk of damage to the delicate flow straightener becomes immense (spoken from experience). Finally, consult Scott Sinquefield before doing anything to the LEFR that may in any way threaten it or its performance. Scott built the reactor and is therefore its foremost authority.

A more extensive study of metals recovery should be made, since results in this study were inconclusive. A reactor with a liquid quench instead of a cooling tube may eliminate the possibility of vaporized metals condensing and sticking to tube walls.

In addition to obtaining solids heating values for various mixtures of black liquor and secondary sludge, it may also be worthwhile to examine the change in water evaporation

requirements when relatively low-solids secondary sludge is added into a recovery

process.

Acknowledgements

Bibliography

Brink, D., Thomas, F., Jones, K., *TAPPI Journal* (May, 1970), Volume 53, Number 5: 837-843.

Cameron, J.H., Grace, T.M., *TAPPI Journal* (July, 1982) Volume 65, Number 7: 84-87.

Cameron, J.H., Grace, T.M. "Kinetic Study of Sulfate Reduction with Kraft Black Liquor Char," *Ind. End. Chem. Fund.* (April, 1985), Volume 82, Number 4: 443-449.

Chai, X.-S., Luo, Q., Zhu, J.Y. "Analysis of Nonvolatile Species in a Complex Matrix by Headspace Gas Chromatography," *Journal of Chromatography*. A 909 (2001): 249-257.

"Chemiluminescent NO/NO$_x$ Analyzer, Model 10AR, Instruction Manual," Thermo Environmental Instruments, Inc.

Flaxman, J., Hallett, W.L.H. "Flow and Particle Heating in an Entrained Flow Reactor," *Fuel* (May, 1987), Volume 66, Number 5: 607-611.

Forssen, M., P. Kilpinen, and M. Hupa, "NOx Reduction in Black Liquor Combustion-Understanding Reaction Mechanisms Reveal Novel Operation Strategy Options," *TAPPI International Chemical Recovery Conference Proceedings* (1998): 747-762.

Frederick, J. "How Integrated Gasification Will Impact Kraft Pulping and Chemical Recovery," *TAPPI Journal* (September 1999), Volume 82, Number 9: 45-47.

Frederick, W.J., Grace, T.M., Joyce, T.W. "Disposal of Secondary Sludge in the Kraft Recovery System," TAPPI Environmental Conference Proceedings. (1980): 43-47.

Frederick, W.J., Iisa, K., and Sricharoenchaikul, V. "Black Liquor Gasification: Is It for Sulfite and NSSC Pulp Mills Too?" *TAPPI Pulping Conference Proceedings*. (1999): 269-277.

Horenziak, Steve. "Examination of Sulfurous Products from the Gasification of Kraft Black Liquor Solids," A190 Research Project Report, Institute of Paper Science and Technology, Atlanta, Georgia, (May 1999).

Iisa, Kristiina, Horenziak, Steven, and Jing, Qun. "Evolution of Gas Phase Sulfur During Gasification of Black Liquor," *TAPPI International Chemical Recovery Conference Proceedings*. (2001): 289-295.

Iisa, K., Q. Jing, J. Conn, N. Rompho, C. Tangpanyapinit, and R. Pianpucktr, "Model for NO Formation in Recovery Boilers," *TAPPI International Chemical Recovery*

Conference Proceedings (1998): 763-776.

Jing, Qun, Freisen, Holly, Torres, Paulette, Iisa, Kristiina, "Combined Gasification of Mill Wastes and Black Liquor," (October, 1999). Unpublished.

Larson, E.D., Yang, W., Iisa, K., Malcolm, E.W., McDonald, G.W., Frederick, W.J., Kreutz, T.G., and Brown, C.A. "A Cost-Benefit Assessment of Black Liquor Gasifier/Combined Cycle Technology Integrated into a Kraft Pulp Mill," *TAPPI International Chemical Recovery Conference Proceedings*. (1998): 1-18.

Li, J., van Heiningen, A.R.P., "Sulfur Emission During Gasification of Black Liquor Char," *International Chemical Recovery Conference Proceedings*. (1989) Ottawa, Canada: 209-216.

McGovern, J.N., Berbee, J.G., Bockheim, J.G., and Baker, A.J. "Characteristics of Combined Effluent Treatment Sludges from Several Types of Pulp and Paper Mills," *TAPPI Journal* (March 1983), Volume 66, Number 3: 115-118.

Oscarsson, B. "Lessons Learned from Gasifier Operating Experience," *TAPPI Journal* (October 1999), Volume 82, Number 10: 46-48.

Schwanz, J.M.M. "The Addition of Secondary Sludge to the Recovery Boiler," A190 Research Project Report, Institute of Paper Science and Technology, Atlanta, Georgia, (May 1999).

Scott, G.M., Abubakr, S., and Smith, A. "Sludge Characteristics and Disposal Alternatives for Recycled Fiber Plants," *TAPPI Recycling Symposium* (1995): 239-249.

Senning, A, Sulfur in Organic and Inorganic Chemistry, (1972). Marcel Dekker Press, New York: 55-57.

Sricharoenchaikul, V., Reis, V.V., Carangal, A., Sinquefield, S.A., Iisa, K., and Frederick, W.J. "Experimental Measurements of the Pyrolysis Products from Black Liquor Using a Laminar Entrained-Flow Reactor," Paper 253c, AIChE Annual Meeting, San Francisco, California, (November 1994).

Strohbeen, D.T., Grace, T.M., *TAPPI Journal* (October, 1982). Volume 65, Number 10: 125-126.

Thompson, Laura M. "The Depletion of Nitric Oxide by Reaction with Molten Sodium Carbonate and Sodium Carbonate/Sodium Sulfide Mixtures," Dissertation, Institute of Paper Science and Technology, Atlanta, Georgia, (January, 1995).

Whitty, Kevin. "Pyrolysis and Gasification Behavior of Black Liquor under Pressurized Conditions," Academic Dissertation, Åbo Akedemi University, Turku, Finland

(1997).

Whitty, Kevin, Nilsson, Anders. "Experience from a High Temperature, Pressurized
Black Liquor Gasification Pilot Plant," *TAPPI International Chemical Recovery
Conference Proceedings*. (2001): 281-287.

Appendix

Raw Data

number	sample (temp, res time, liq conc) (deg C, sec, %)	GC file ID	retention time	IA (integrated area) of sample (carbonate)	IA_{sample} - IA_{blank} (carbonate)	Na_2CO_3 in vial (g)	soln concentration (g sample/g soln)	wt frac Na_2CO_3 in char/fume	wt frac carbonate C in char/fume	wt frac total C in char/fume
1	700/0.2/85	490	6.400	182.7	174.4	0.000890	0.007930175	0.281	0.032	0.285
2	700/0.2/90	488	6.399	213.9	205.6	0.001023	0.007930175	0.323	0.037	0.278
3	700/0.2/95	485	6.400	330.1	321.8	0.001518	0.007930175	0.479	0.054	0.254
4	700/0.2/100	493	6.393	238.7	230.4	0.001129	0.007930175	0.356	0.040	0.282
5	900/0.2/85	498	6.378	360.3	352.0	0.001647	0.007930175	0.519	0.059	0.286
6	900/0.2/90	511	6.368	342.1	333.8	0.001569	0.007930175	0.495	0.056	0.279
7	900/0.2/95	487	6.398	335.5	327.2	0.001541	0.007930175	0.486	0.055	0.258
8	900/0.2/100	489	6.389	367.5	359.2	0.001677	0.007930175	0.529	0.060	0.270
9	700/0.7/85	508	6.371	323.2	314.9	0.001489	0.007930175	0.469	0.053	0.260
10	700/0.7/90	506	6.368	345.8	337.5	0.001585	0.007930175	0.500	0.057	0.250
11	700/0.7/95	494	6.381	346.4	338.1	0.001587	0.007930175	0.500	0.057	0.280
12	700/0.7/100	499	6.379	395.5	387.2	0.001796	0.007930175	0.566	0.064	0.273
13	900/0.7/85	512	6.364	376.4	368.1	0.001715	0.007930175	0.541	0.061	0.213
14	900/0.7/90	492	6.383	391.4	383.1	0.001779	0.007930175	0.561	0.064	0.193
15	900/0.7/95	504	6.382	202.4	388.2	0.001801	0.007930175	0.568	0.064	0.238
16	900/0.7/100	503	6.370	420.5	412.2	0.001903	0.007930175	0.600	0.068	0.195
17	700/1.2/85	495	6.379	353.9	345.6	0.001619	0.007930175	0.510	0.058	0.249
18	700/1.2/90	501	6.374	359.6	351.3	0.001644	0.007930175	0.518	0.059	0.248
19	700/1.2/95	496	6.379	376.1	367.8	0.001714	0.007930175	0.540	0.061	0.300
20	700/1.2/100	502	6.370	426.1	417.8	0.001927	0.007930175	0.607	0.069	0.243
21	900/1.2/85	510	6.370	414.2	405.9	0.001876	0.007930175	0.591	0.067	0.130
22	900/1.2/90	500	6.368	494.0	485.7	0.002216	0.007930175	0.699	0.079	0.145
23	900/1.2/95	491	6.381	466.9	458.6	0.002101	0.007930175	0.662	0.075	0.162
24	900/1.2/100	509	6.365	471.2	462.9	0.002119	0.007930175	0.668	0.076	0.153

wt frac organic C in char/fume	char wt. (g)	fume wt. (g)	char + fume wt. (g)	liq fed (g)	liq feed rate (g/min)	wt frac total C in feed liq	wt total C fed (g)	wt total C in char+fume (g)	wt carbonate C in char+fume (g)
0.253	1.805	0.0547	1.860	2.506	0.278	0.304	0.762	0.530	0.059
0.241	1.213	0.0317	1.244	1.698	0.217	0.305	0.518	0.346	0.045
0.200	1.550	0.0224	1.572	2.129	0.258	0.303	0.645	0.399	0.085
0.242	1.392	0.0289	1.421	1.908	0.239	0.299	0.570	0.401	0.057
0.227	1.292	0.0486	1.341	2.190	0.274	0.304	0.666	0.383	0.079
0.223	1.107	0.0359	1.143	1.811	0.244	0.305	0.552	0.319	0.064
0.203	1.418	0.0439	1.462	2.229	0.279	0.303	0.675	0.377	0.080
0.210	1.439	0.0629	1.502	2.282	0.266	0.299	0.682	0.406	0.090
0.207	1.729	0.0575	1.787	2.460	0.273	0.304	0.748	0.465	0.095
0.193	1.689	0.0347	1.724	2.359	0.255	0.305	0.719	0.431	0.098
0.223	2.001	0.0526	2.054	2.797	0.311	0.303	0.847	0.575	0.116
0.209	1.561	0.0546	1.616	2.182	0.242	0.299	0.652	0.441	0.104
0.152	1.466	0.0186	1.485	2.504	0.276	0.304	0.761	0.316	0.091
0.129	1.349	0.0203	1.369	2.324	0.258	0.305	0.709	0.264	0.087
0.174	1.142	0.0204	1.162	1.900	0.211	0.303	0.576	0.277	0.075
0.127	1.032	0.0141	1.046	1.733	0.193	0.299	0.518	0.204	0.071
0.191	1.315	0.0313	1.347	2.044	0.287	0.304	0.621	0.335	0.078
0.189	1.503	0.0359	1.539	2.297	0.311	0.305	0.701	0.382	0.090
0.239	1.271	0.0241	1.296	1.903	0.254	0.303	0.577	0.389	0.079
0.174	1.325	0.0296	1.355	1.961	0.249	0.299	0.586	0.329	0.093
0.062	1.155	0.0437	1.199	2.053	0.294	0.304	0.624	0.155	0.080
0.066	1.201	0.0325	1.233	2.211	0.259	0.305	0.674	0.179	0.098
0.086	1.502	0.0395	1.541	2.686	0.313	0.303	0.814	0.249	0.116
0.077	1.458	0.0500	1.508	2.433	0.279	0.299	0.727	0.230	0.114

wt organic C in char/fume	% total C fed recovered as organic C	% total C fed volatilized	frac char recovery (g char/g fed) (original)	frac fume recovery (g fume/g fed)	wt frac total S in feed	wt% S in char	wt S fed (g)
0.471	0.618	0.304	0.721	0.022	0.05350		0.134
0.300	0.580	0.332	0.714	0.019	0.05373		0.091
0.314	0.487	0.381	0.728	0.011	0.05397		0.115
0.343	0.602	0.297	0.730	0.015	0.05420		0.103
0.305	0.458	0.424	0.590	0.022	0.05350		0.117
0.255	0.461	0.423	0.611	0.020	0.05373		0.097
0.297	0.439	0.442	0.636	0.020	0.05397		0.120
0.316	0.463	0.406	0.631	0.028	0.05420		0.124
0.370	0.494	0.379	0.703	0.023	0.05350		0.132
0.333	0.463	0.401	0.716	0.015	0.05373		0.127
0.459	0.541	0.321	0.716	0.019	0.05397		0.151
0.337	0.517	0.324	0.715	0.025	0.05420		0.118
0.225	0.296	0.585	0.585	0.007	0.05350		0.134
0.177	0.250	0.627	0.580	0.009	0.05373		0.125
0.202	0.351	0.520	0.601	0.011	0.05397		0.103
0.133	0.256	0.606	0.595	0.008	0.05420		0.094
0.257	0.413	0.461	0.644	0.015	0.05350	3.02	0.109
0.291	0.416	0.455	0.654	0.016	0.05373		0.123
0.309	0.537	0.326	0.668	0.013	0.05397		0.103
0.236	0.402	0.439	0.676	0.015	0.05420	3.11	0.106
0.075	0.120	0.751	0.563	0.021	0.05350	1.86	0.110
0.081	0.120	0.735	0.543	0.015	0.05373		0.119
0.133	0.164	0.694	0.559	0.015	0.05397		0.145
0.116	0.159	0.684	0.599	0.021	0.05420	2.35	0.132

wt S in char (g)	%S fed volatilized	mols total C fed	mols S fed	molar feed rate total C (mol/min)	molar feed rate S (mol/min)	COS$_{ppm}$	%feed S recovered as COS
		0.063	0.004	0.007	0.00046	13	3.1
		0.043	0.003	0.006	0.00036	13	4.0
		0.054	0.004	0.007	0.00043	14	3.5
		0.048	0.003	0.006	0.00040	14	3.8
		0.055	0.004	0.007	0.00046	13	3.2
		0.046	0.003	0.006	0.00041	15	4.0
		0.056	0.004	0.007	0.00047	15	3.4
		0.057	0.004	0.007	0.00045	14	3.4
		0.062	0.004	0.007	0.00046	14	3.3
		0.060	0.004	0.006	0.00043	13	3.5
		0.071	0.005	0.008	0.00052	14	3.0
		0.054	0.004	0.006	0.00041	14	3.7
		0.063	0.004	0.007	0.00046	19	4.7
		0.059	0.004	0.007	0.00043	16	4.1
		0.048	0.003	0.005	0.00036	16	5.1
		0.043	0.003	0.005	0.00033	15	5.2
0.04067	62.80117	0.052	0.003	0.007	0.00048	17	3.9
		0.058	0.004	0.008	0.00052	18	3.8
		0.048	0.003	0.006	0.00043	19	4.9
0.04213	60.35885	0.049	0.003	0.006	0.00042	18	4.7
0.02230	79.69858	0.052	0.003	0.007	0.00049	30	6.7
		0.056	0.004	0.007	0.00043	22	5.6
		0.068	0.005	0.008	0.00053	23	4.8
0.03543	73.12329	0.061	0.004	0.007	0.00047	25	5.7

H_2S_{ppm}	%feed S recovered as H_2S	$MeMerc_{ppm}$	%feed S recovered as MeMerc	$n\text{-prop}_{ppm}$	%feed S recovered as n-propMerc	%feed S recovered overall	NOx_{ppm}	wt frac N in feed (from Schwanz)
125	29.7	43	10.2	8	1.9	45.0	8	0.0026471
136	41.3	32	9.6	11	3.4	58.4	5	0.0025
139	35.2	41	10.3	9	2.2	51.3	2	0.0007368
216	58.8	48	13.0	16	4.4	80.1	1	0.0007
154	37.1	33	8.1	9	2.3	50.6	11	0.0026471
141	38.1	15	4.0	8	2.0	48.1	9	0.0025
176	41.4	29	6.8	16	3.7	55.4	3	0.0007368
231	56.7	47	11.7	25	6.1	77.9	2	0.0007
149	36.0	37	9.0	13	3.2	51.5	17	0.0026471
157	40.5	25	6.5	6	1.6	52.1	14	0.0025
206	43.4	37	7.8	10	2.2	56.4	5	0.0007368
236	63.4	40	10.8	11	3.1	81.0	3	0.0007
146	35.0	9	2.2	8	2.0	43.9	18	0.0026471
144	36.7	6	1.6	5	1.4	43.8	14	0.0025
130	40.3	7	2.1	5	1.5	49.1	4	0.0007368
131	44.3	5	1.7	6	2.0	53.2	3	0.0007
271	62.3	15	3.5	5	1.3	71.0	16	0.0026471
285	60.3	10	2.2	5	1.1	67.3	13	0.0025
362	93.3	7	1.9	8	1.9	102.0	5	0.0007368
322	84.2	15	3.9	7	1.9	94.7	4	0.0007
399	89.6	7	1.6	15	3.4	101.3	20	0.0026471
251	63.8	8	2.0	9	2.2	73.6	14	0.0025
230	48.1	6	1.2	14	2.8	56.9	6	0.0007368
370	86.6	5	1.2	10	2.4	95.9	5	0.0007

g N fed per minute feed	mols N fed per minute	%feed N recovered as NOx	%feed N recovered as ammonia
0.0007369	5.2637E-05	16.8	25.8
0.0005419	3.8709E-05	13.7	21.0
0.0001904	1.36E-05	13.0	20.0
0.0001674	1.1958E-05	7.4	11.4
0.0007245	5.1748E-05	23.9	36.7
0.0006096	4.3541E-05	22.3	34.3
0.0002053	1.4664E-05	24.1	37.0
0.0001859	1.3281E-05	13.3	20.4
0.0007234	5.167E-05	35.9	55.2
0.0006368	4.5488E-05	33.0	50.7
0.000229	1.6354E-05	32.4	49.8
0.0001697	1.2122E-05	29.1	44.8
0.0007303	5.2165E-05	38.9	59.9
0.0006454	4.6101E-05	32.5	50.1
0.0001556	1.1111E-05	39.7	61.1
0.0001348	9.6278E-06	36.7	56.4
0.0007599	5.4281E-05	32.5	50.0
0.0007781	5.5582E-05	25.4	39.1
0.0001873	1.3377E-05	39.6	60.9
0.0001746	1.2469E-05	35.4	54.4
0.000779	5.5639E-05	39.7	61.0
0.0006468	4.6199E-05	32.5	50.0
0.0002308	1.6488E-05	42.8	65.9
0.0001955	1.3966E-05	37.9	58.3

Carbonate Data

number	sample (temp, res time, liq conc) (deg C, sec, %)	GC file ID	retention time	IA (integrated area) of sample (carbonate)	IA$_{sample}$ - IA$_{blank}$ (carbonate)	Na$_2$CO$_3$ in vial (g)
25	#1 calibration	497	6.385	237.7	229.4	0.001124
26	#2 calibration	486	6.391	455.0	446.7	0.002050
27	#3 calibration	507	6.349	721.2	712.9	0.003183
28	#4 calibration	505	6.334	1001.7	993.4	0.004378
blank	blank	484	6.382	8.3		

calibration curve data		
solid Na$_2$CO$_3$ (g)	wt frac Na$_2$CO$_3$ in calibration solution	Na$_2$CO$_3$ in vial (g)
0.265	0.002643268	0.001057307
0.535	0.005322632	0.002129053
0.8125	0.008062044	0.003224818
1.0925	0.010811479	0.004324592

Mass Na$_2$CO$_3$ in Sample vs. Peak Area

$y = 234820x - 34.644$

$R^2 = 0.9974$