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AN EMPIRICAL EQUATION OF THE VOLATILIZATION OF KRAFT
BLACK LIQUOR DROPLETS DURING BURNING

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ABSTRACT

Kraft black liquor burning phenomena were studied in a
convective single particle reactor. The droplets were suspended
from a microbalance in a downward flowing hot gas stream. The
linear portion of the mass loss history during the burn mainly
corresponded to the volatiles burning stage. An empirical rate
equation was determined statistically from the normalized slope of
this linear region. Included in the equation were initial droplet
size and gas phase oxygen concentration. The mass loss rate was
closely proportional to the initial droplet surface area. Gas
temperature was not found to be statistically significant.

INTRODUCTION

Chemical recovery is an integral part of the kraft pulp-
ing process because it regenerates the cooking chemicals. Pulping
produces both pulp and a weak black liquor containing organics and
inorganics. The pulp continues on to the papermaking process.
The weak black liquor is concentrated into strong black liquor
which is then combusted in the recovery boiler. The organic

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fraction is oxidized for steam generation which is used millwide. The inorganic fraction is reduced to recover Na_2S, a pulping chemical, and Na_2CO_3, in the form of smelt. The smelt dissolves in an aqueous stream to form green liquor which is then causticized; the conversion of Na_2CO_3 into NaOH. The regenerated cooking chemicals, Na_2S and NaOH, then return to the digester for more pulping.

Very little quantitative information is known concerning the fate of black liquor droplets in the recovery boiler. The stages that the droplet experiences were identified by Hupa (1985) and Grace (1985). The three main burning stages are drying, volatiles burning, and char burning.

The drying stage is evaporation of water in the black liquor as a result of heat transferred to the droplet. The volatiles burning stage consists of three major processes: volatiles evolution, volatiles combustion, and the formation of char in an inorganic matrix. A great deal of swelling and bursting occurs during the drying stage, with sustained swelling only during the volatiles burning stage. The char is then consumed during the char burning stage. When the carbon content is sufficiently low the char structure collapses, and the inorganics, in the form of molten smelt, coalesce. The stages overlap slightly, especially in the larger droplets. For this work, visual events were used to

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define the beginning and the end of each stage. These techniques will be discussed later.

Single droplet studies done with black liquor at The Institute of Paper Chemistry (IPC) (Miller 1986, Moreland 1985, and Robinson 1986) suggested several variables important to black liquor combustion. These were droplet temperature, droplet initial size, gas temperature, and gas composition. Research done on single droplets (Hupa 1985) combusted each droplet in a radiantly heated stagnant air environment and measured the times for each stage. Hupa's times will be compared with those from this investigation.

The present investigation had two goals. The first was to determine an empirical equation for the linear region of the droplet mass loss history and the second was to define what occurred in this region.

EXPERIMENTAL

The apparatus used for this work can be seen in Figure 1. It is a convective downflow single particle reactor. The gas is heated in an electrical furnace, travels through an insulated pipe, passes through a flow straightener, and enters the single particle reaction area. The flow rate of the gas is adjustable.

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There is a damper to divert the gas flow while the sample is placed in the reactor. The sample is suspended on a wire connected to the electronic microbalance. The microbalance and the gas analyzers are connected to an Apple II+ microcomputer with an analog/digital interface. Heat transfer to the sample is primarily through convection, with some radiative heat transmitted from the surrounding walls. A 16 mm motion picture is taken of each burn through the optical trench. The times for each stage of the burn are obtained from the movies.

(Figure 1 here)

At the start of each burn the kraft black liquor is weighed and wrapped around the wire. The black liquor, from Thilmany Pulp and Paper Co., Kaukauna, WI, had been concentrated to 71.8% solids under vacuum. The black liquor is shaped into an approximate sphere. A wire coil and screen, the basket, surrounds the sample to provide constant drag throughout the burning, as the drop does not swell uniformly. Once the drop has been formed, the reactor is opened by lowering the lower section, the damper is closed to divert the hot gas, the sample in the basket is hooked onto the microbalance wire, the reactor is closed, the 16 mm motion picture camera is started, and the computer is started. The computer causes the damper to open, allowing the hot gas to reach the sample at a defined time zero. The camera runs for up .

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to 16 seconds, while the data acquisition program runs for 20
seconds.

The experimental design was based upon the central-
composite-rotatable three-variable statistical design. This
design examined the effects of reactor temperature, T, (660 to
860°C), initial mass of the droplet, M_i, (4 to 41 mg), and oxygen
content in the gas stream, O_2, (0 to 21%), on the rate of vola-
tiles evolution. Replications were done at the center point
(10.5% O_2, 763°C, 22 mg) to determine the lack of fit and the
reproducibility of the data. The design assumes that the lack of
fit is constant for all conditions.

<div align="center">RESULTS</div>

Droplet Mass Loss

The plot of the mass of the droplet over time for a typi-
cal burn can be seen in Figure 2. The initial rise in the curve
is due to the microbalance adjustment to the drag force on the
basket and wire assembly. Mass loss data does not reflect the
burning process for approximately the first second. The slope of
the linear region is the rate of mass loss during the volatiles
burning stage, the primary rate measurement used in this work.

<div align="center">(Figure 2 here)</div>

For the purpose of data consistency the following stage transition points were defined. Drying started the moment the droplet was exposed to the hot gases, and ended at the first visual evidence of ignition. The droplet was assumed to be 100% solids at ignition, although residual moisture contents of 5 to 10% are possible. Volatiles burning started at ignition and ended at the point of maximum swollen volume. Maximum volume usually occurred near the end of the linear mass loss. Char burning started at maximum volume and ended at the final collapse of the char structure into a smelt bead.

The points of ignition, maximum volume, and smelt coalescence are noted on the plot. The droplet ignited initially near the wire under all the tests except those at 0% O_2. At 0% O_2 the particle was under pyrolysis conditions and did not ignite or combust. After the volatiles burning stage, mass is continuously lost as carbon is consumed. The weight regain noted prior to the smelt bead formation is due to reoxidation of Na_2S formed during the burning processes (Grace, 1985).

Linear Mass Loss Rate

The slope of the linear region SL, during the volatiles burning stage, was found by linear regression through the included points. It was normalized with respect to initial liquor solids.

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$$NSL = SL / (SOL * M_i) \qquad (1)$$

where SOL is the initial solids fraction and

M_i is the initial droplet mass in mg.

This was done so that particles of different size could be directly compared. The diameter, D_i, was calculated from the density of black liquor and the mass of the droplet. The droplet was assumed to be a perfect sphere. When data are plotted for a single oxygen content, as in Figure 3 at 10.5% O_2, the plot is linear with minimal scatter. The equation for the line is

$$NSL = 1.04 - 0.242\ D_i \qquad (2)$$

with an r^2 of 0.80. A plot of SL vs. diameter was much more scattered. Figure 4 shows the plot of NSL against D_i for all the data. Each of the five gas compositions tested is plotted separately. The scatter is partially due to the variation of temperature in the gas stream, T, in which the burns were done. When all the burns were combined the statistical equation was

$$NSL = \frac{1.634}{D_i} + 0.034\ \frac{O_2}{D_i} - 0.0054\ O_2 - 0.316 \qquad (3)$$

with an r^2 of 0.85. O_2 is the percent oxygen in the bulk gas stream. This equation was determined using stepwise linear

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regression from a statistical software package for IBM or compatibles. Each variable was entered in the equation depending on its F-test value. New F-test values were calculated after each step. After all the variables with F-test values high enough to enter the equation were entered, the program stepped backward, removing all the variables with F-test values below the F-to remove value. Only one variable was entered or removed from the equation per step. The interaction terms O_2/D_i, D_i*O_2, D_i*T, and O_2*T, were included to test the variable interactions. D_i*O_2, D_i*T, O_2*T, and T were not statistically significant.

(Figure 3 and 4 here)

NSL was obtained according to equation (1) by dividing the rate of mass loss by the initial mass, M_i. This is equivalent to dividing by the cube of the initial diameter, D_i, and a constant. This means that in equation (3), the rate of mass loss is proportional to the square of D_i. In other words, the rate of mass loss during volatiles burning is dependent on the initial surface area of the droplet.

Figure 5 shows the comparision of model to data. The other two levels of oxygen, 4.3% and 16.7%, behaved in a similar manner. They were not included on the plot to improve clarity. Figure 6 shows the agreement between the statistical equation and the data.

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(Figure 5 and 6 here)

It was not too surprising that the reactor temperature was not a significant variable. Hupa (1985) had found only a slight influence of reactor temperature on the volatiles burning time. In both this work and that of Hupa the temperature of the particle surface, the reaction zone, was not measured. Its relationship to the volatiles burning rate may be a more significant temperature to measure.

Times

The times for drying, volatiles burning, and char burning are listed in Table 1. Hupa's (1985) times are compared to the ones from this work for a 23 mg droplet, 3.08 mm in diameter, combusted in air. Hupa presented his findings in plots with the largest initial droplet 2.0 mm in diameter. His times were graphically extrapolated and should only be considered as an estimate. The difference in droplet sizes is due to the necessity of comparing burns under similar combustion conditions.

Even though Hupa's times can only be taken as an estimate, they are significantly longer than the present data. One reason for the difference in the drying times is that Hupa had much more water to dry. Hupa's liquor was 60% solids and this

work was at 71.8% solids. Another reason for the difference is
that Hupa had a lower heat flux in the furnace than the present
work, 76 kW/m^2 compared to 87 kW/m^2 based on rough calculations
and experimental verification for IPC's flux (Miller 1986).

Table 1. Comparision of Movie to Hupa Times for the Combustion of
          a 3.08 mm Diameter Droplet

| | Time (sec) | |
	Movie	Hupa
Drying	1.7	3.8
Volatiles Burning	2.8	4.2
Char Burning	3.5	5.0
Total	8.0	13.0

The volatiles burning time is 50% longer. The above fac-
tors are expected to influence the drying region but do not
explain the differences in the volatiles burning region. External
diffusion of oxygen through the bulk gas or differences between
the liquors may have contributed to the different times. If dif-
fusion was important, then changing the velocity of the gas stream
from stagnant (Hupa) to flowing (present) would reduce the times
for this stage by having higher net O_2 content at the particle
surface. It is not possible at this stage to comment on differ-
ences between the two liquors.

DISCUSSION

The present results provide the first data on mass loss rates during the volatiles burning stage for a black liquor droplet. They are, however, insufficient to support a quantitative explanation of the controlling phenomena. The data suggest that the initial droplet surface area is a key factor in the volatiles burning stage. Since the actual surface area is continually changing, the data do not differentiate between external or internal controlling processes. Externally controlled kinetics (i.e., through the gas temperature) had no significant effect. Externally controlled mass transfer (i.e., the O_2 content), or possibly the O_2 concentration effect on the reaction kinetics, did slightly influence the mass loss rate during volatiles burning. Future measurements of dynamic surface area and temperature should help clarify relative rates of external and internal processes.

CONCLUSIONS

Several conclusions can be drawn from this preliminary work. The first is that the linear region in the droplet's mass loss history mainly corresponds to the volatiles burning stage. The second is that the rate of mass loss in the linear region is closely proportional to the surface area of the initial droplet. Quantification of particular rate limiting steps for the volatiles

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burning region will require future work. Finally, for closely similar reactor conditions, Hupa's volatile burning times (1985) were longer than those from this work. Differences in air flow rate past the particles appear to be an important difference between these works.

Portions of this work were used by (KAC) as partial fulfillment of the requirements for the Master of Science degree at The Institute of Paper Chemistry.

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Robinson, M. Characterization of Black Liquor Droplet Drying in Air, Steam, and Humid Air. Doctorate Thesis in Progress. Appleton, WI, The Institute of Paper Chemistry, 1986.

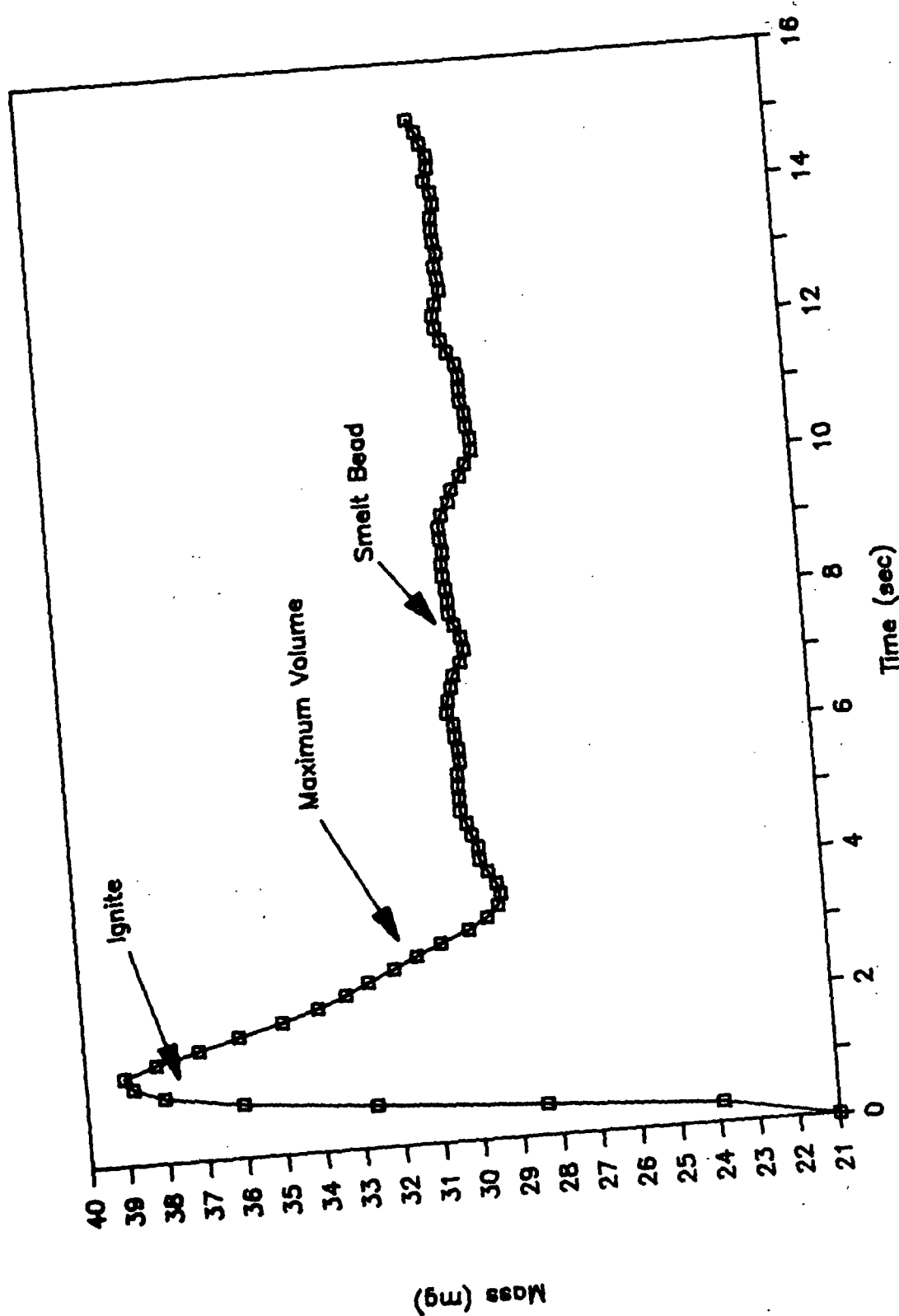# SINGLE PARTICLE REACTOR
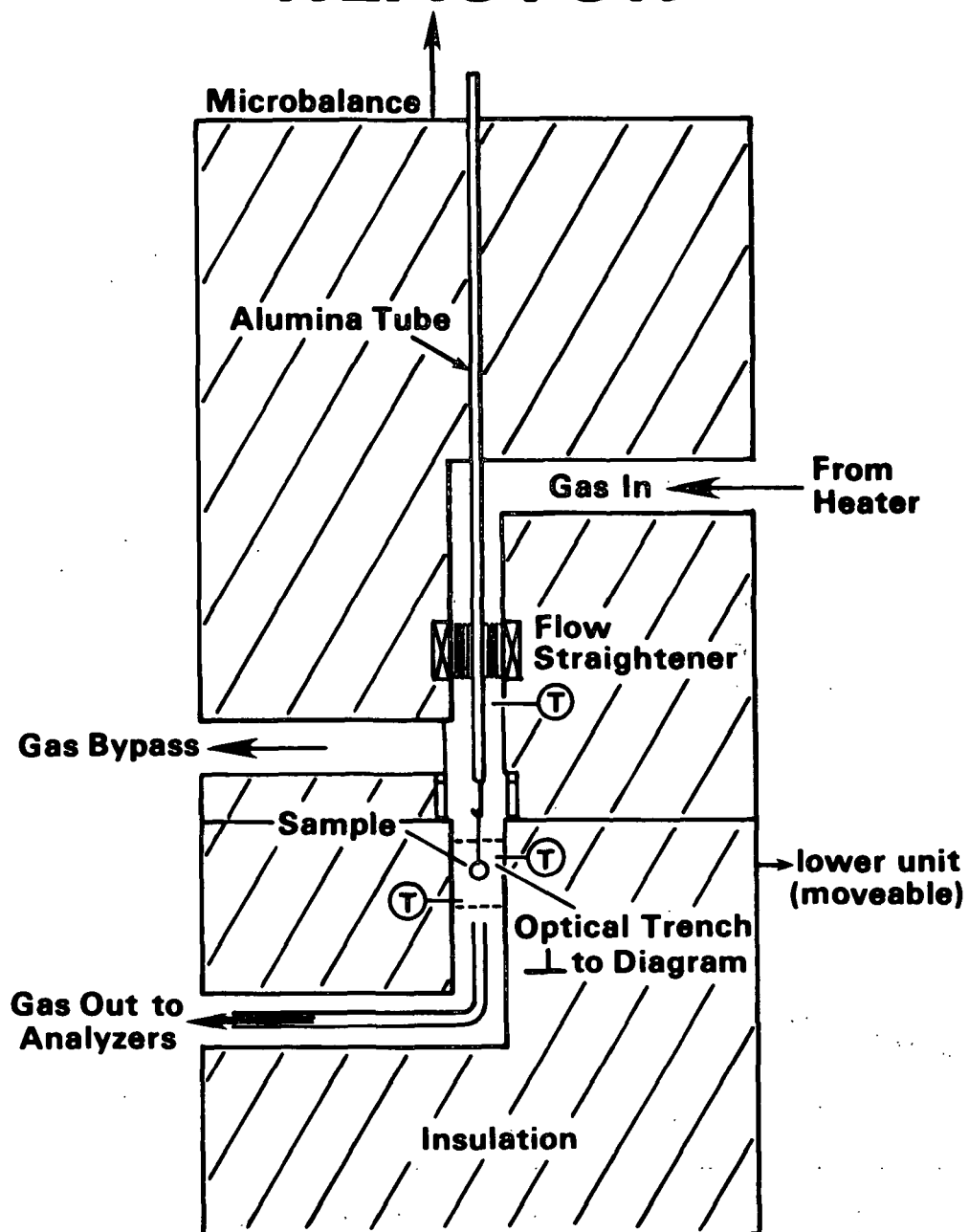
Figure 1. Single Particle Reactor.

Figure 2. Black Liqour Droplet Mass History. Sample – 21 mg at 71.8% Solids, Gas – 10.5% O_2 Balance N_2 at 763°C.
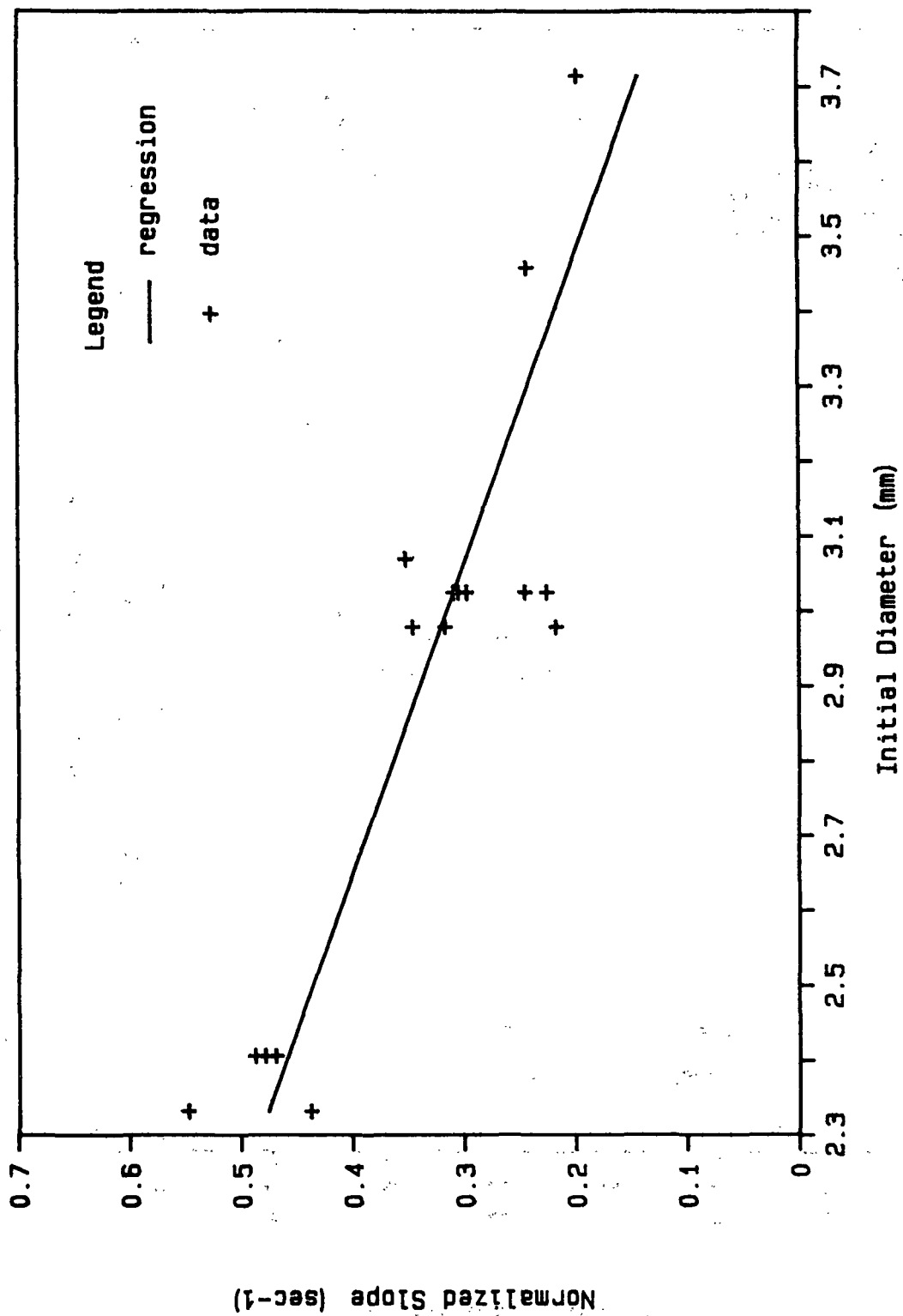
Figure 3. Normalized Rate vs. Initial Diameter for Conditions of 10.5% O_2.
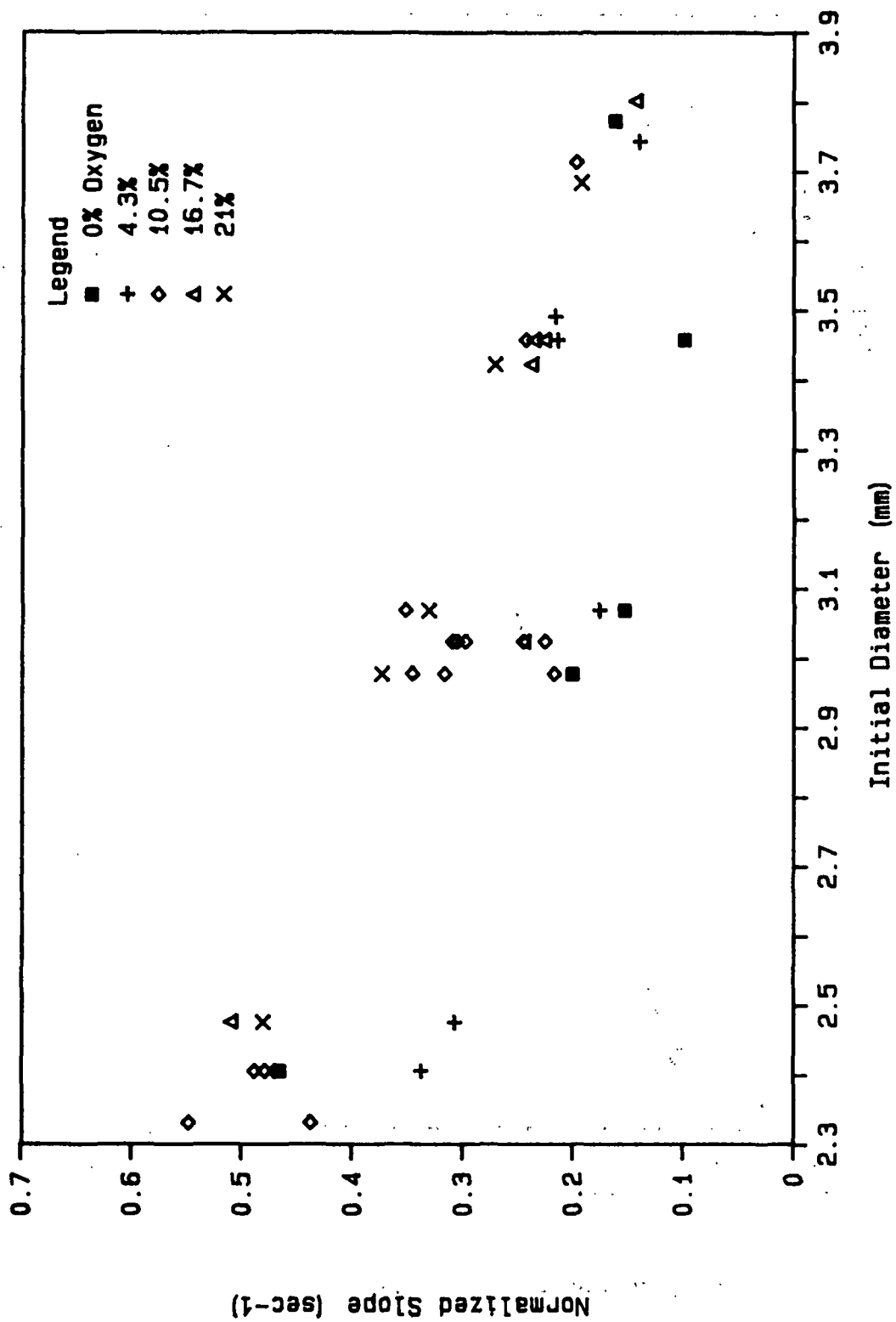
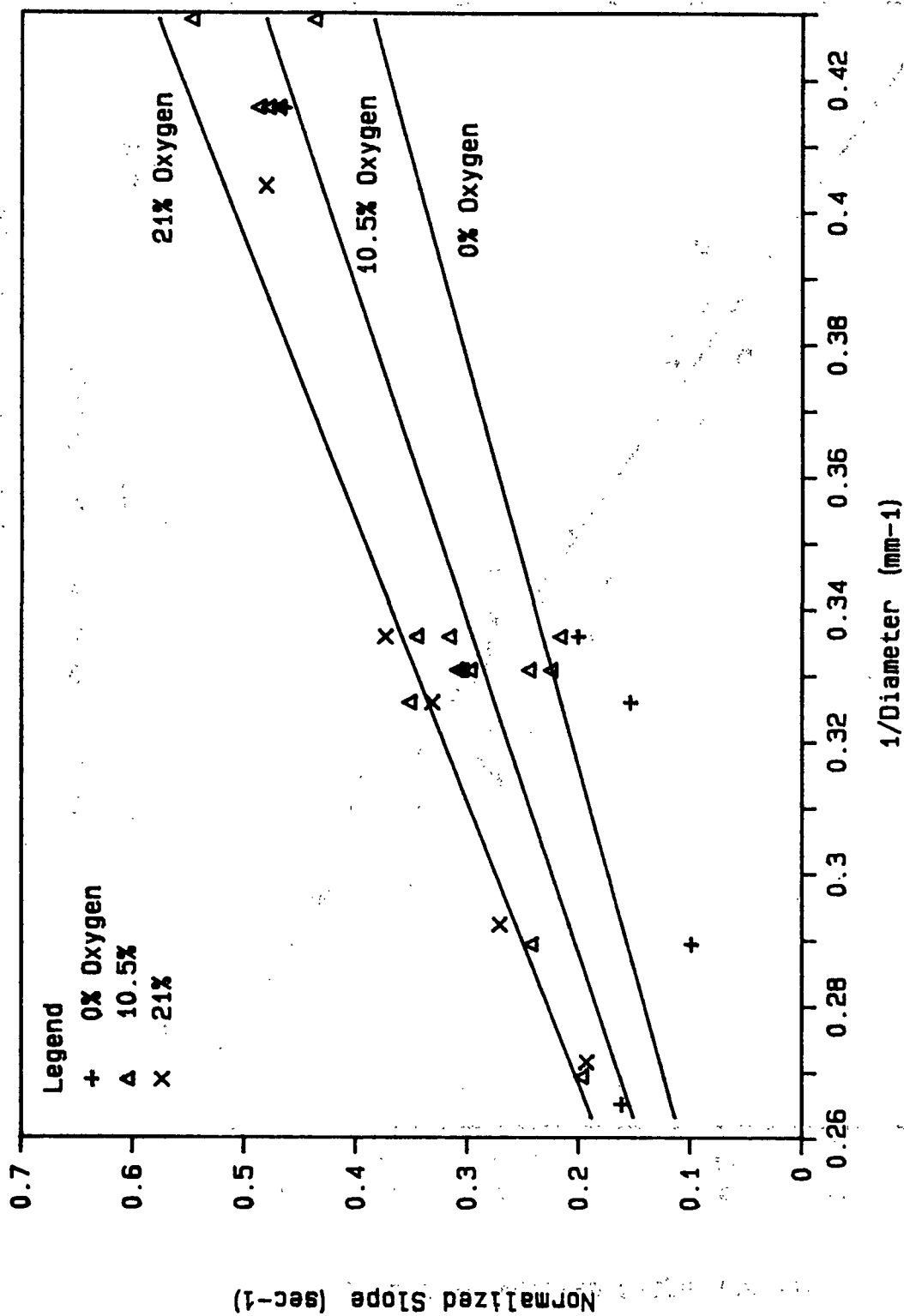Figure 4. Normalized Rate vs. Initial Diameter for all Data.

Figure 5. Comparison of Statistical Model (Equation 2) with
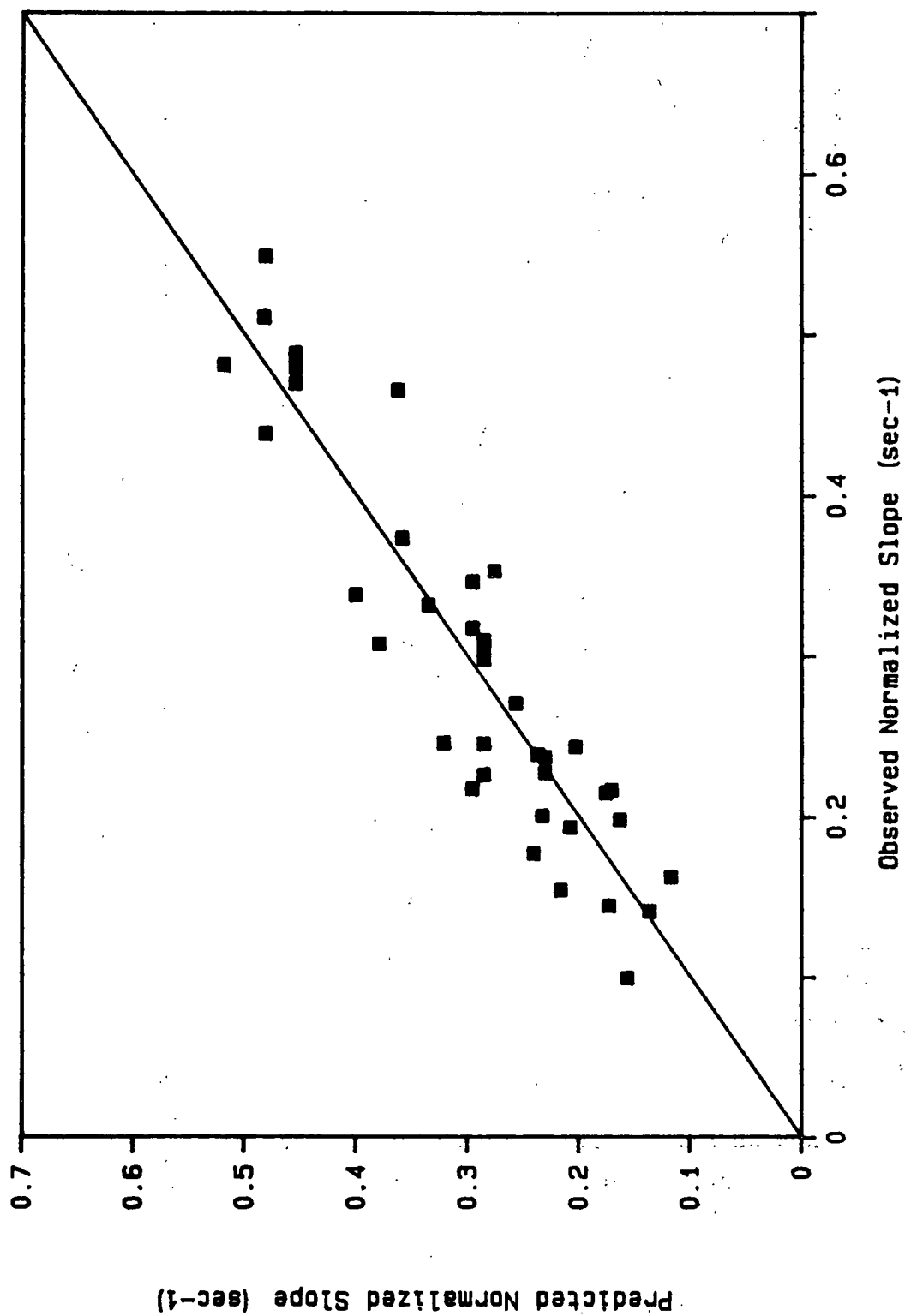the Experimental Data at Three Oxygen Levels.

Figure 6. Predicted vs. Observed Normalized Mass Loss Rate.