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STRUCTURE AND THERMOCHEMICAL KINETIC STUDIES OF COAL PYROLYSIS

Contract No.: DE-FG22-90PC90296

QUATERLY TECHNICAL PROGRESS REPORT

Period: October 1 - December 31, 1991

Prepared by: Joseph N.D. Dodoo, Principal Investigator

Consultant: Martin Hertzberg

DOE Project Manager: Phouc X. Tran

Submitted to:

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O.Box 10940, Pittsburgh,PA. 15236

By:

Department of Natural Sciences
University of Maryland Eastern Shore
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A Century of Progress Through Teaching, Research and Extension

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PROJECT OBJECTIVES

The overall objectives of this project is an intensive effort on the application of laser to the microscopic structure and thermochemical kinetic studies of coal particles pyrolysis,char combustion and ash transformation at combustion level heat fluxes in a laser beam. Research emphasis in FY91 is placed on setup and calibration of the laser pyrolysis system,preparation and mass loss studies of Beulah lignite and subbituminous coals. The task is therefore divided into three subtasks.

SUBTASK 1 SETUP AND CALIBRATION OF THE LASER SYSTEM

During the early part of FY91, considerable time and effort were expended in a complete overhaul of the Co_2 Model C41 laser. The exercise was necessary in order to reestablish the full operational capabilities of the laser. New sets of mirrors and lenses were installed and realigned. The power meter was calibrated against a modern COHERENT Labmaster power meter. In April, a consignment of standard,well-characterized and protected coal samples was received from the National Coal Repositories at Argonne National Laboratory and Penn State University.

SUBTASK 2 ABSORPTION RATE DATA FOR BEULAH ZAP LIGNITE

Objective: To obtain data for mass increase due to absorbed moisture for the Beulah Zap lignite and other subbituminous coals.

Deliverables: A comprehensive data on the rate of absorption of moisture by the lignite and subbituminous coals from their initial dry state.

The coal examined is DECS-11 (North Dakota Beulah Zap lignite). The samples from the Penn State Coal Sample Bank were prepared and kept in an inert atmosphere prior to shipping. Proximate analysis of the sample is shown in Table 1.

	As Rec'd %	Dry %
Moisture	33.38	
Volatile matter	37.36	56.08
Fixed carbon	22.89	34.36
Ash	6.37	9.56

Table 1 Proximate analysis of the Beulah lignite.

Throughout the course of these studies the coal samples were kept inside a glove box under inert,dry atmosphere. The glove box also housed a balance and a hot plate for thoroughly drying the coal samples prior to pyrolysis measurements. A COMPU-TRAC Moisture Analyzer was employed to carry out the first of a series of moisture absorption studies. The COMPU-TRAC moisture analyzer combines the simplicity of thermogravimetric moisture measurement with accurate control and computational facilities to accurately determine the moisture content of any solid. Approximately 3 - 4 gram of coal sample were used in each case.

Extreme caution was exercised to ensure that the coal samples were maintained under the same condition as existed at preparation and shipping. The coal bag was opened under inert atmosphere inside the glove box. Once the required amount had been taken out the bag was resealed with a strong adhesive tape. The removed coal was then carried in a closed vial out of the glove box through the double door hatch. The drying process was initiated immediately upon removing the coal from the glove box by carefully depositing the powder onto the COMPU-TRAC pan. The amount of moisture in the sample was displayed at the end of the drying process. The 34% mass loss obtained corresponded with the analyzed moisture content of the coal. As soon as the sample was dried it was removed and allowed to stand unprotected inside the laboratory. Wight measurements were obtained at half hourly intervals for 6.5 hours.

The measurements were repeated in an inert environment inside the glove box. A hygrometer provided a record of the humidity inside the glove box which was carefully controlled. The drying was accomplished with the aid of the hot plate heating at a nominal temperature of 120 °C. A heating period of about 30 minutes was generally sufficient to achieve the analyzed moisture content of the coal. The dried sample was kept inside the glove box for several hours with corresponding mass increase recorded at half hourly intervals. When the series of measurements was completed the glove box was completely flushed with N_2 at a rate of 300 cm^3/s for two hours releasing a volume of gas equivalent to five times the volume of the glove box. Figure 1 shows the increase in mass due to absorbed moisture by the Beulah lignite. Large increases in mass accompany high humidity values. At 62% relative humidity the coal mass increases by 5.5% in the first half hour rising to 8.5% in another half hour. The increase is somewhat lower ,6.3% at the end of one hour for a humidity of 52% but the first half hour shows the same increase in mass. For both 44% and 30% relative humidities the absorbed moisture is less over a

long period. Half an hour after drying the increase in mass in both cases is 3.4%. One hour after drying the value is about 4%. The values for the first one hour after drying provide a most useful information for this project. A typical preparation and laser heating requires up to between 15 to 20 minutes. The humidity inside the laboratory was maintained below 50% at all times. Thus the samples pyrolyzed were considered dry.

SUBTASK 2. MASS LOSS STUDIES OF BEULAH LIGNITE

Preliminary pyrolysis measurements on Beulah lignite at a flux of 200 W/cm^2 for about 1 second were found to be consistent with the 56% ASTM volatility listed for this dried coal. Moreover, the particles did not fragment under these conditions. The variation of the devolatilization weight loss with time at different flux amplitudes for Beulah lignite is shown in Figs. 2 and 3. The weight loss versus time histories were obtained by applying the same laser beam intensity to a set of particles with average diameter 70 μm, but of increasing duration. The laser pressure was maintained at a steady state value of 13.5 mm Hg throughout the measurements. In Fig.2 the particles were exposed in (a) N_2 environment and (b) air medium. In Figs.3 and 4 the devolatilization weight loss is shown for are shown flux values of 262 W/cm^2 and 315 W/cm^2;and 228 W/cm^2 and 300 W/cm^2 respectively. The data for flux values of 228 and 262 W/cm^2 are presented in Table 2. Both sets of data were recorded under nitrogen environment. These early results indicate that at short exposure periods the heating wave is over before it has had time to propagate through the entire width of the average particle. The particles rest on an aluminum substrate which in turn rests on a water cooled orifice plate directly below the beam. The weight loss at shorter exposure periods is thus small, generally lower than the listed ASTM volatility. The trend is linear and the data show little scatter.

At longer exposure periods much scatter is observed in the data. The wave front is no doubt propagating through the entire width of the average particle. The devolatilization is rapid but here again the effect of quenching from the substrate cannot be overlooked. Some particles may be quenched more than the rest while others, in the same ensemble,may be heated rather more. Another possible cause for the scatter could be non-uniform heating of the particles. We would like to think that every precaution is taken to ensure uniform distribution of particles and also uniform heating. We intend to carry out a series of runs,each represented by a data point,at the same heating flux but of increasing duration. This,we hope, should resolve the scatter observed at longer exposure periods. Tar condensation was observed with the lignite. The amount of tar deposited increased with increasing exposure times and beam intensity.

PLANS FOR NEXT YEAR

The devolatilization weight loss studies will be extended to both the bituminous and subbituminous coals. The particles to be studied will be confined to the size range 50 μm and below. SEM/X-ray studies of both tar and ash from the devolatilized particles will also be investigated. Char burnout studies will also be carried out to provide direct correlation of weight loss measurements during heterogeneous char oxidation. In early January, 1992 some of the results of our studies on these low-rank coals will be presented at the International Conference on Heterogeneous Combustion at the Dead Sea, Israel. The work leading to this conference and the continuing studies will be the subject of the first quarterly report in 1992.

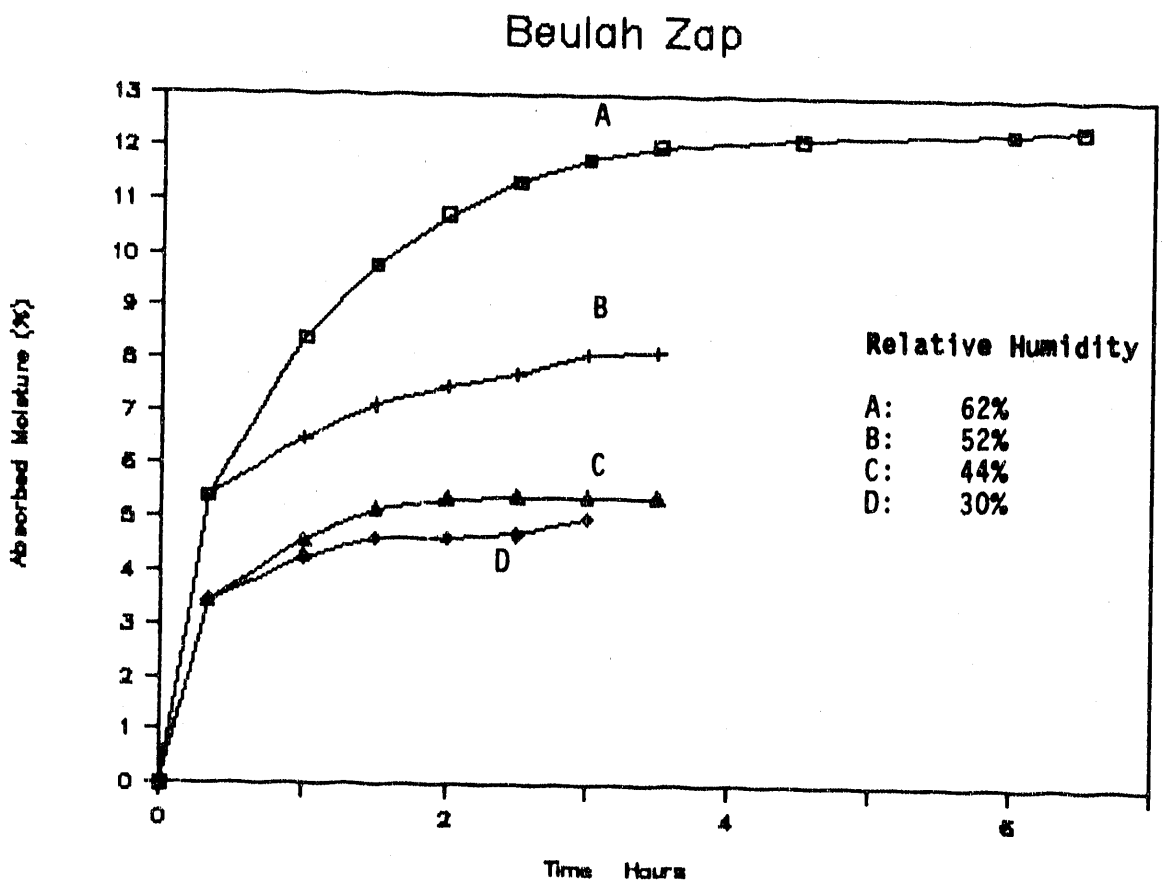
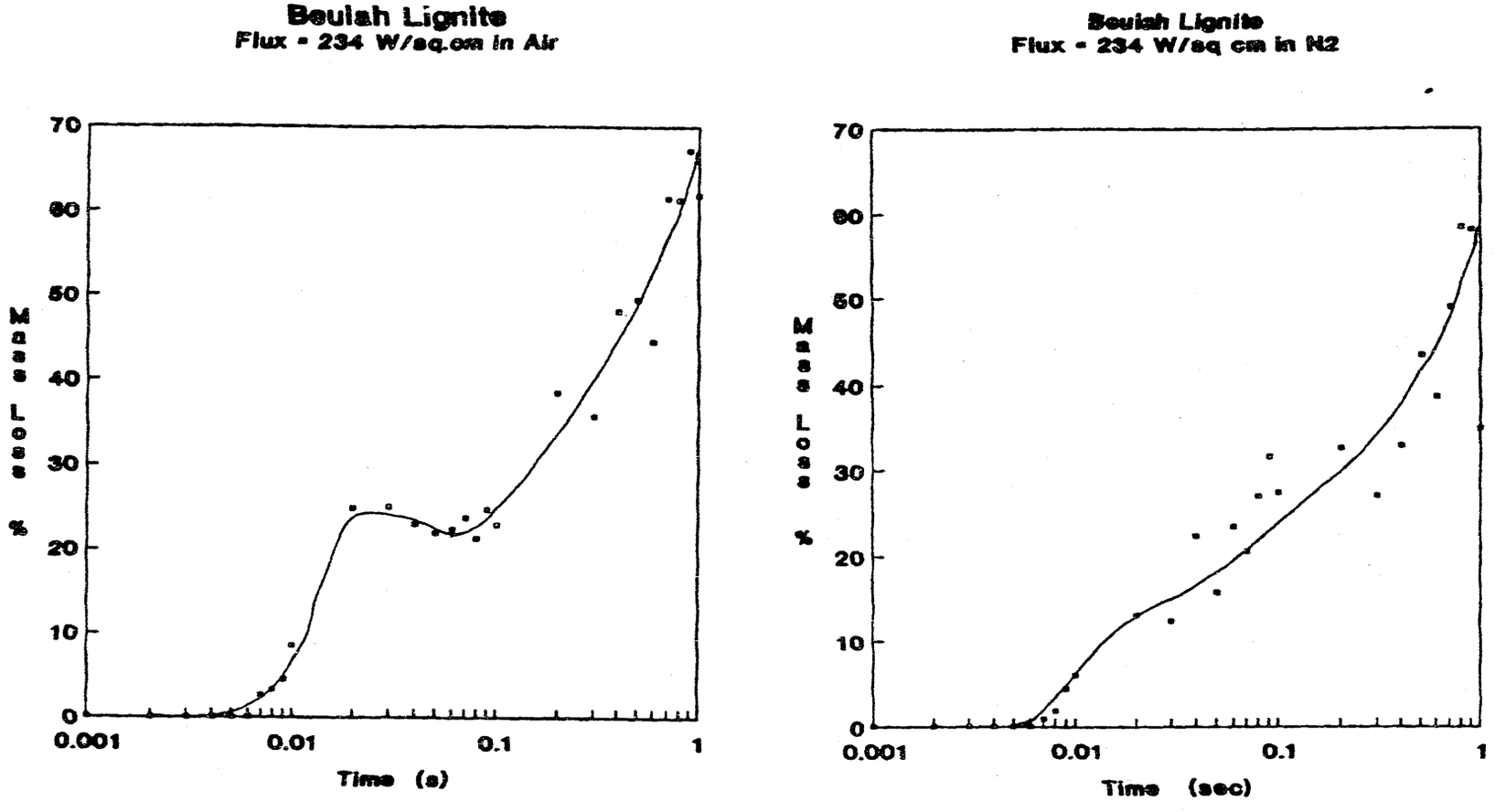
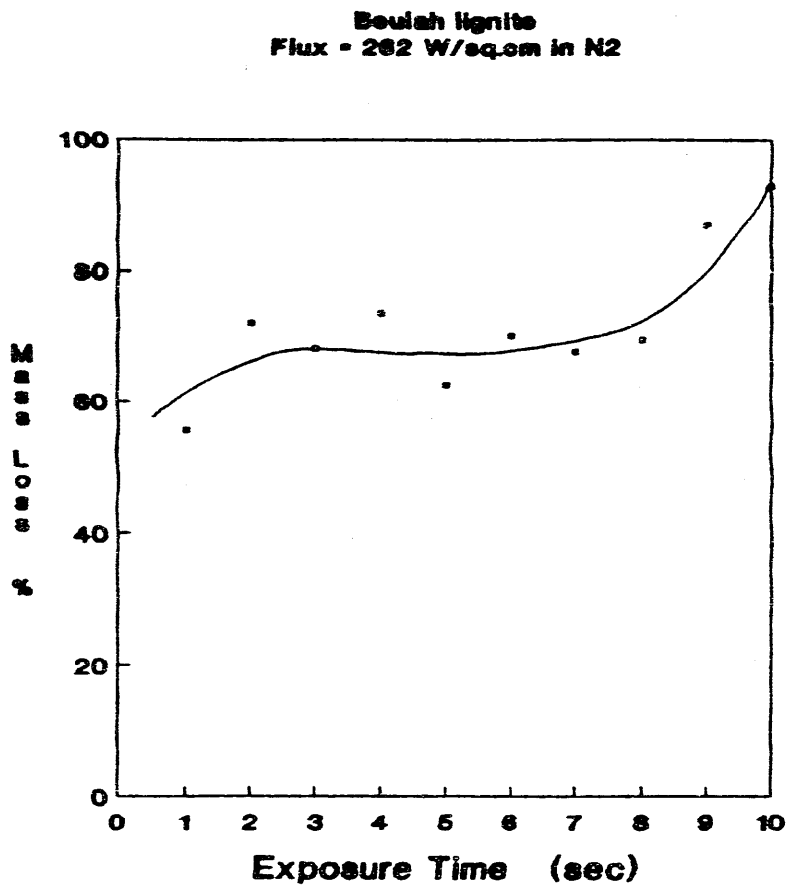


Fig. 1. Increase in mass due to moisture absorption by the Beulah Zap lignite. A; inside the laboratory, B thru D; inside an inerted atmosphere of a glove box.

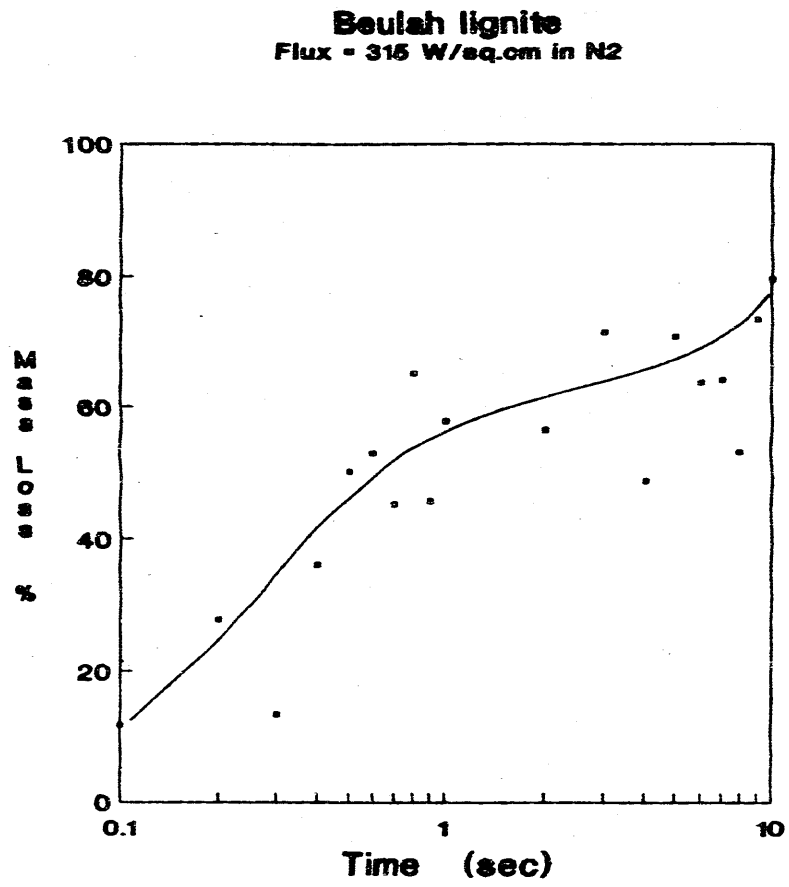


(a) (b)

Fig. 2. Effect of time on devolatilization weight loss from Beulah lignite. The laser intensity was 234 W/cm$_2$ in (a) nitrogen environment and (b) air medium.

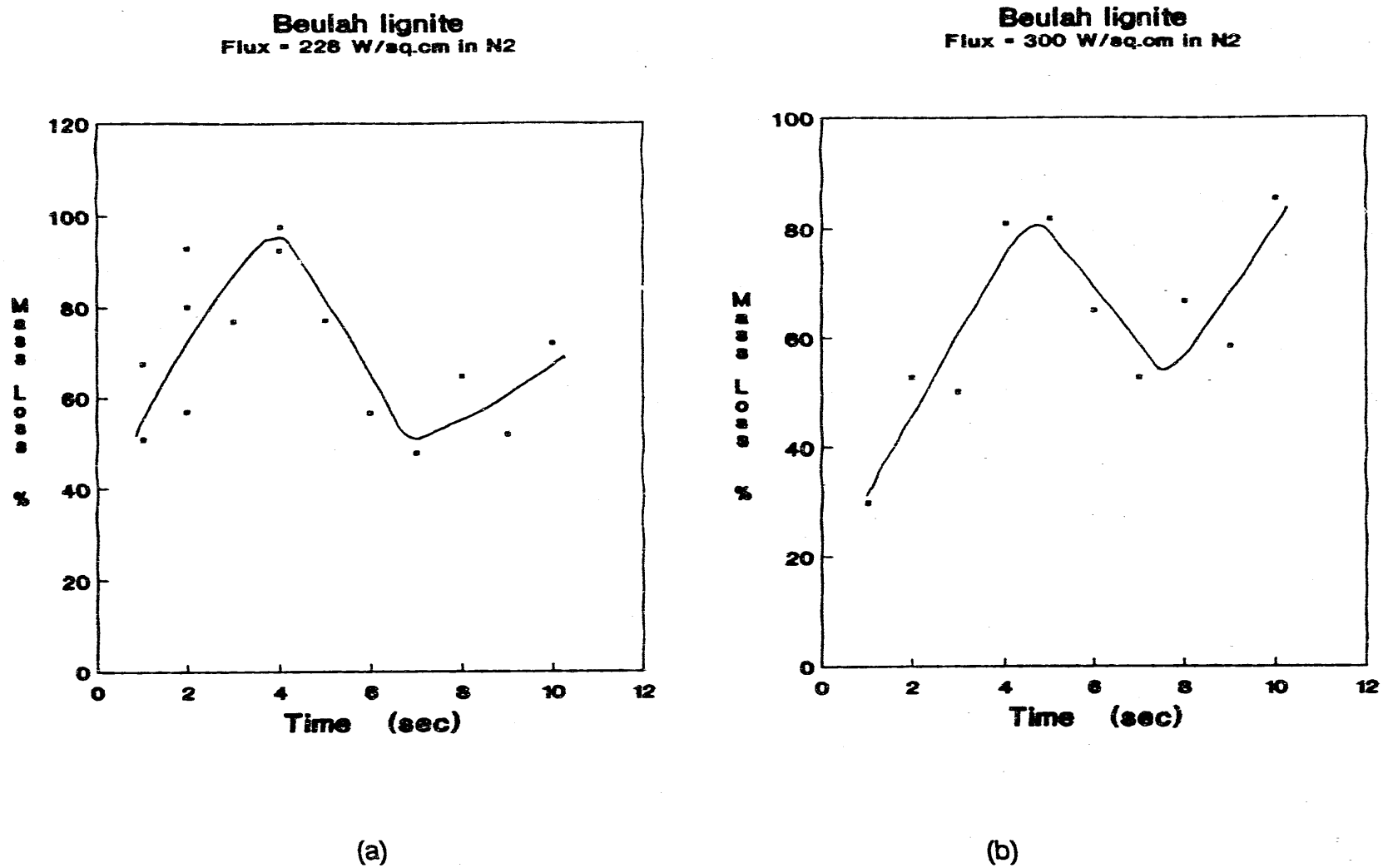


(a)



(b)

Fig. 3. Effect of time on devolatilization weight loss from Beulah lignite at (a) 262 W/cm^2 and (b) 315 W/cm$_2$ in nitrogen environment.



(a) (b)

Fig. 4. Effect of time on devolatilization weight loss from Beulah lignite at (a) 228 W/cm^2 and (b) 300 W/cm$_2$ in nitrogen environment.

Table 2a

Exp. Time (s)	Mass (μg)	Δm (μg	% Loss
1	19.0	12.8	67.4
2	7.4	4.2	56.6
3	4.3	3.3	76.7
4	7.8	7.2	92.3
5	2.6	2.0	76.9
6	2.3	1.3	56.5
7	4.6	2.2	47.8
8	3.1	2.0	64.5
9	14.7	7.6	51.7
10	26.6	19.1	71.8

Table 2b

Exp. Time (s)	Mass (μg)	Δm (μg)	% Loss
1	1.8	1.0	55.6
2	5.7	4.1	71.9
3	6.9	4.7	68.1
4	8.3	7.2	92.3
5	4.0	2.5	62.5
6	3.0	2.1	70.0
7	3.4	2.3	67.6
8	4.9	3.4	69.4
9	4.6	4.0	87.0
10	2.8	2.6	92.9

Table 2. Mass loss for Beulah lignite in N_2 environment with a flux of (a)228 W/cm^2 and (b) 262 W/cm^2

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