# Engineering the Production of Hydrogen to Biomass via Catalytic Steam Reformer: Pyrolysis

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August 17, 2001

Prepared in partial fulfillment of the requirements of the Department of Energy ERULF Program under the direction of Dr. Bob Evans in the Field Test Laboratory Building at the National Renewable Energy Laboratory.

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# Abstract

**Engineering in the Production of Hydrogen from Biomass via Catalytic Steam Reformer: Pyrolysis. MALENE A. SAVAGE (Clark Atlanta University, Atlanta, GA 30314) Dr. Robert Evans (National Renewable Energy Lab Golden, CO 80401).**

Many efforts have been made to produce a competitive alternative to natural gas. Natural gas lowers the pollution but it is expensive and limited. One leading idea is that of renewable hydrogen. Renewable hydrogen has the potential of being cost effective and environmental friendly. The strategy is based on producing hydrogen from biomass pyrolysis using a co-product strategy to reduce the cost of hydrogen. During the first steps slow pyrolysis is used to maximize the yield of charcoal using densified peanut shells. Results were produced using the molecular beam mass spectrometer and the differential scanning calorimeter. MBMS produced kinetic data analysis that will help in predicting time and temperature requirements. The DSC produced information needed for heat requirements. All of the data gained from this summer will be used in the planning of the project.

ERULF: Engineering

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## Introduction

The chronic problems we have today concerning energy supply and demand are becoming unbearable. Not only have prices skyrocketed in recent years, but emissions also have started to become more of a health issue. There has been an attempt to lower the pollution by using natural gas; however, natural gas is expensive and supplies are limited. One goal of renewable energy research is to produce a competitive alternative to natural gas. One leading idea is renewable hydrogen. Renewable hydrogen has the potential of being cost effective and is environmentally friendly. Integrating hydrogen production with existing industrial utilization of agricultural residues can speed the use of hydrogen.

Organizations are working in Georgia to develop a steam reforming process for making hydrogen from agriculture residues such as peanut shells (Abedi, 2001). The organization team consists of National Renewable Energy Lab, Clark Atlanta University (CAU), Scientific Carbons Inc. (SCI), Enviro-Tech Enterprises, Inc. (ETI), and Georgia Institute of Technology (GT). CAU is assisting in the combustion science, environmental science, and the developments of steam reforming. SCI is a company that makes activated carbon from agricultural residues. ETI is a company whose goal is to establish partnerships to create jobs via sustainable technology. GT is applying capabilities in systems analysis, environmental and energy technologies. These groups are examining the byproducts of a process for making activated carbon from densified peanut shells (Chornet et al, 1994, 2001). The scaled-up fluid bed reactor based on NREL research has been built and will be interfaced with the 10-20 kg/hr fluidized-bed pyrolysis system at NREL for shakedown (Evans, 2001). The reactor will then be shipped to Georgia for interfacing with the SCI plant. The hydrogen produced by the scale up reactor will be blended with compressed natural gas and used to power a bus in Albany, Georgia. This strategy will demonstrate how hydrogen and bioenergy are economically feasible and can foster the development of rural areas when practiced on a larger scale. The production of renewable hydrogen from biomass, which is a chemically complexed renewable resource, requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas.

The objectives of the NREL work are: (1) to design the 10 kg/hr fluid bed catalytic steam reformer system; (2) to conduct the system shakedown by interfacing with the Thermochemical Process Development Unit (TCPDU) in the Thermochemical User's Facility (TCUF) located on NREL's campus; (3) to participate in the design of the process modifications that will be necessary to integrate the reactor safely and efficiently in the existing Scientific Carbon process; (4) to support the partnership development that will be necessary for the bus demonstration; (5) to identify with biomass resources in the region that could be used to produce hydrogen in conjuction with the Scientific Carbon process or by using other integrated biomaterial processing technologies.

The process of catalytic steam reforming began at NREL in 1993 (Chornet et al, 1994). The strategy is based on producing hydrogen from biomass pyrolysis using a co-product strategy to reduce the cost of hydrogen. The original plan was to divide the pyrolysis oil in to two fractions based on the water solubility; the insoluble fraction can be used in adhesive formulation. While this technology continues to move forward commercial practice is still some time in the future. The process of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product that is practiced commercially. During the first step of the activated carbon process, slow pyrolysis is used to maximize the yield of charcoal producing organic vapors in 40% yield. A slipstream of these pyrolysis vapors will be used for the long duration of the steam-reforming tests that will occur in Georgia.

There is growing need for zero emission fuels in Atlanta, Georgia. There are several public transportation buses that are currently running on natural gases. Since Atlanta has growing air quality problems these buses are helping to minimize the problem. Zero emission fuels like hydrogen can be used in those same fleets by blending with natural gas. Although this is process is still very expensive, it has great potential for cities like Atlanta.

This project is very important to the world for many reasons. It will allow polluted cities to begin to clean up their air and would be a less expensive way for the cities population to get around. In time the renewable hydrogen will be economically feasible as well as environmentally friendly.

## Materials and Methods

To determine the optimum conditions for pyrolysis of densified peanut shells several lab-scale tests were performed. Experiments with cellulose were also performed as a reference. Since much work has been done in the past using the experimental work, the work was done on the Molecular Beam Mass Spectrometer. The Differential Scanning Calorimeter was used to determine the reaction kinetics and heat requirements.

### *Molecular Beam Mass Spectrometer*

The first instrument used was the Molecular Beam Mass Spectrometer (MBMS). The MBMS is based on a three stage, differentially pumped vacuum system. During the testing process both the peanut shells and the cellulose pyrolysis products ionized with an electron beam detected with a quadrupole mass filter which separates the ions by molecular weight.

The next instrument used was the Differential Scanning Calorimeter. The DSC measures temperatures and heat flows that are associated with thermal transitions in material.

*Molecular Beam Mass Spectrometer Testing*

During the **MBMS** runs approximately 300 milligrams of each sample, cellulose or densified peanut shells, were placed in a small quartz and placed into a flow tube at a set temperature between 300◦C and 500◦C. Flowing helium swept the products of pyrolysis from the tube where they were expanded into the MBMS sampling system. Plotting total ions versus time monitored the real time evolution of products. Reaction rates were calculated by assuming first order kinetics during the isothermal portion of the experiment that is from 50% to 75% of the total product evolution profile.

*Differential Scanning Calorimeter*

During the testing in the DSC, a small aluminum pan consuming approximately 30 milligrams of each sample was placed in the instrument next to a reference pan. The sample was rapidly heated with nitrogen at a set temperature between 300◦C and 500◦C. These isothermal runs were used to compare the endothermic portion due to heat transferred and product volatilization and the subsequent exothermic portion due to char reactions.

## Results

*MBMS Test*

Peanuts 350

Figure 1 shows peanut pyrolysis at 350◦C. The bell curve, which is the total ion intensity, shows the rate of volatile product evolution. Integrating the curve by taking the negative natural log of the fraction converted is used to estimate the rate of pyrolysis.

Peanuts 400

Figure 2 shows peanut pyrolysis at 400C. By comparing both figure 1 and figure 2 we can see that at the higher temperature the reaction is completed quicker because of the higher heating rate.

*DSC Test*

Cellulose

Figure 3 shows the heat flow versus the time. In this graph we can see how when starting from room temperature the sample began to take in heat, which is an endothermic process. Once devolatilization is complete, exothermic process then began and heat is actually generated. By comparing studies of cellulose the actual heat balances can be calibrated and used as a basis for the results for other materials. That work is to be pursued in the future.

Peanuts

Shown here in figure 4 are two examples of data from the DSC. Both graphs show the process is exothermic because of the amount of heat that was generated. At 350C the exothermic process was slightly larger than that at 400C. A different data analysis technique is needed to know why and will be explored in the future.

## *Batch Reactor (Char Yield)*

Peanuts 25 min

The data presented in figure 5 shows the char yield versus temperature ranges from 300C to 500C. The graph shows experimental error and the regression line, which shows a decrease in the char yield by the temperature range.

## Discussion and Conclusions

Each test performed demonstrated the approach to be followed in systematically studying the fundamentals of the pyrolysis process to be used in Georgia. Methods for building an empirical model of a carbonization reactor were developed and demonstrated. The molecular beam mass spectrometer produced kinetic data analysis that will help in predicting time and temperature requirements. The differential scanning calorimeter produced information needed for the heat requirements. There is still a lot of work to be done. Slow pyrolysis will continue here at NREL until the catalyst is shipped to Georgia. The kinetic analysis methods used are also under development. Cellulose will be used to calibrate rates to correct temperature accuracy. More than one product group (e.g. cellulose and lignin) will be used to produce data from time- resolved kinetics. There is a need to develop different data analysis techniques for the DSC along with more model systems to calibrate the instrument response. All data produced this summer will be used in the planning of the project. The worked completed here answered some questions but opened the door for a lot more.

## Acknowledgements

I thank the United States Department of Energy for providing me with a solid opportunity to further my knowledge and gain experience working in engineering and chemistry.  I also would like to thank the National Renewable Energy Lab and its employees especially Linda Lung who helped tremendously in my stay here in Colorado and at NREL.  Special thanks to my mentor, Dr. Bob Evans for all of his guidance, patience, and enthusiasm with this project.  Lastly, I would also like to thank the ERULF program and AWU for sponsoring me.

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Figure 1:

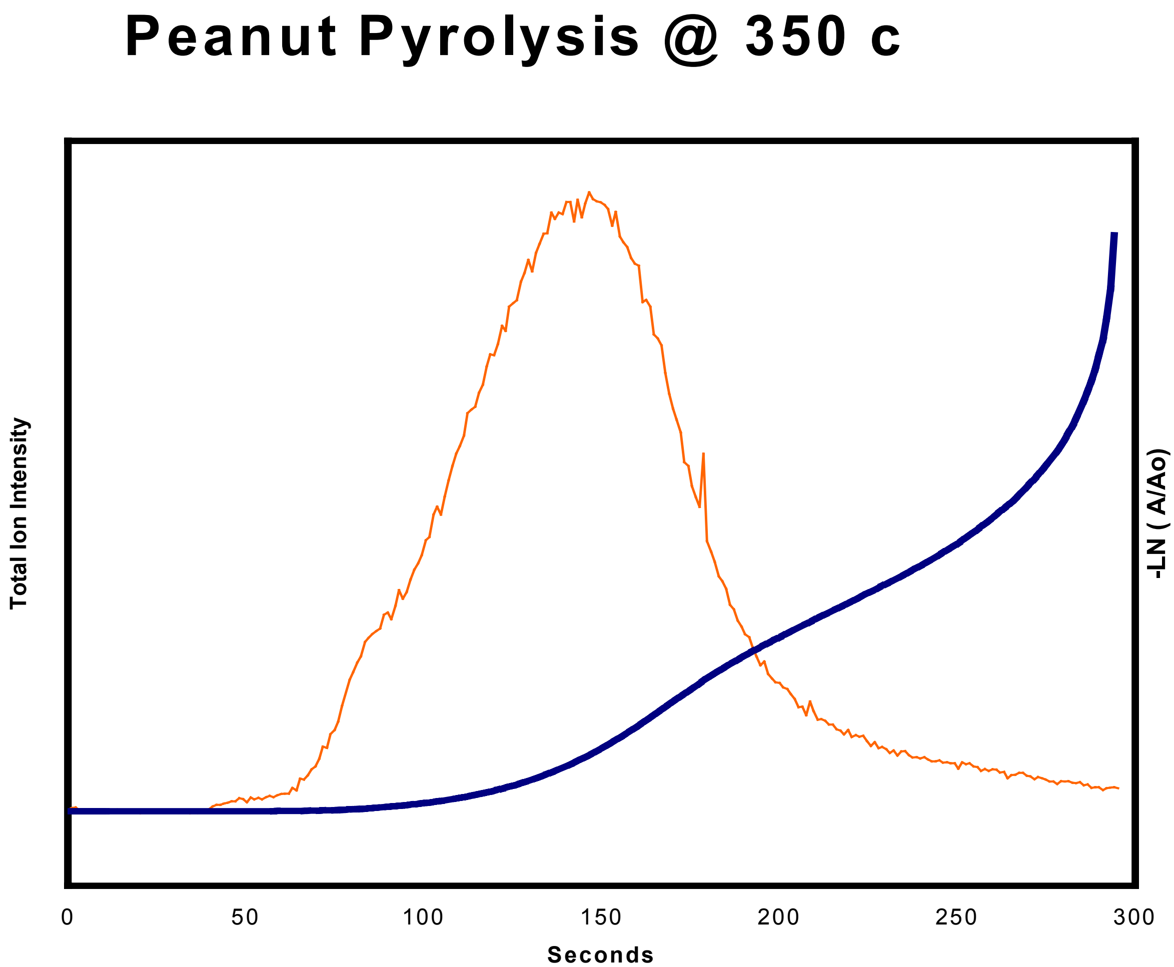

Peanut Pyrolysis @ 350 c
Total Ion Intensity
-LN ( A/Ao)
0
50
100
150
200
250
300
Seconds

Figure 2:

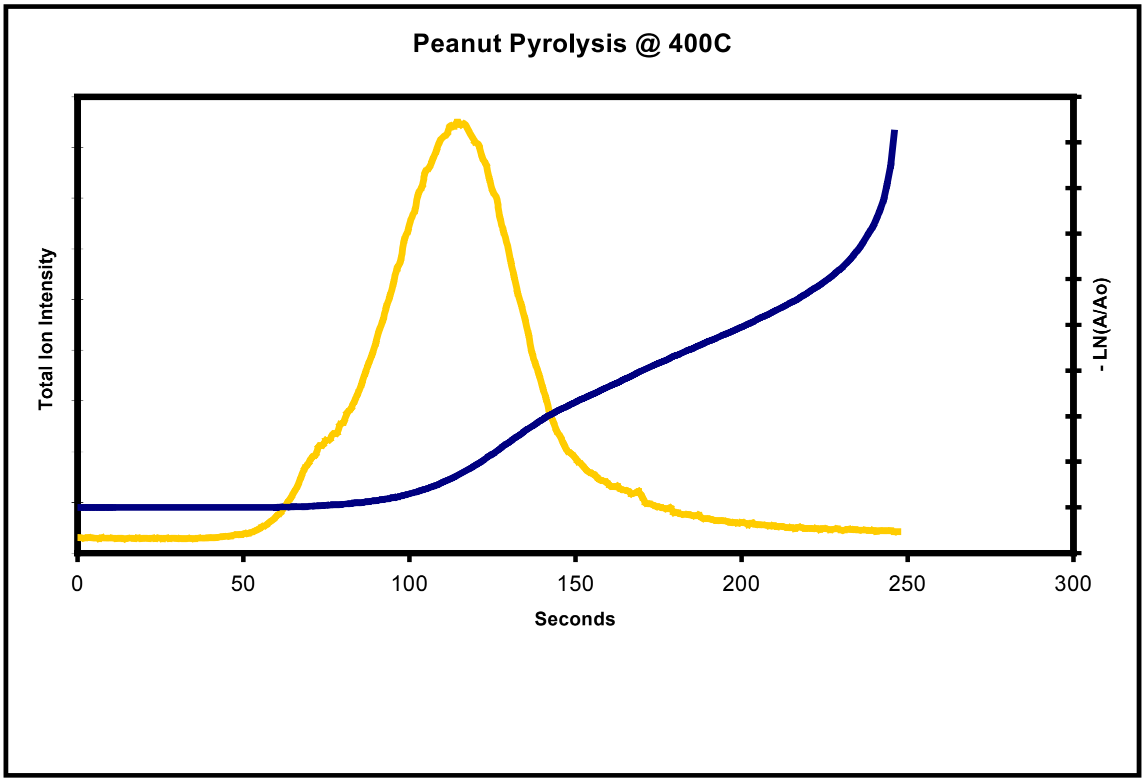

Peanut Pyrolysis @ 400C
Total Ion Intensity
- LN(A/Ao)
0
50
100
150
200
250
300
Seconds

Figure 3:

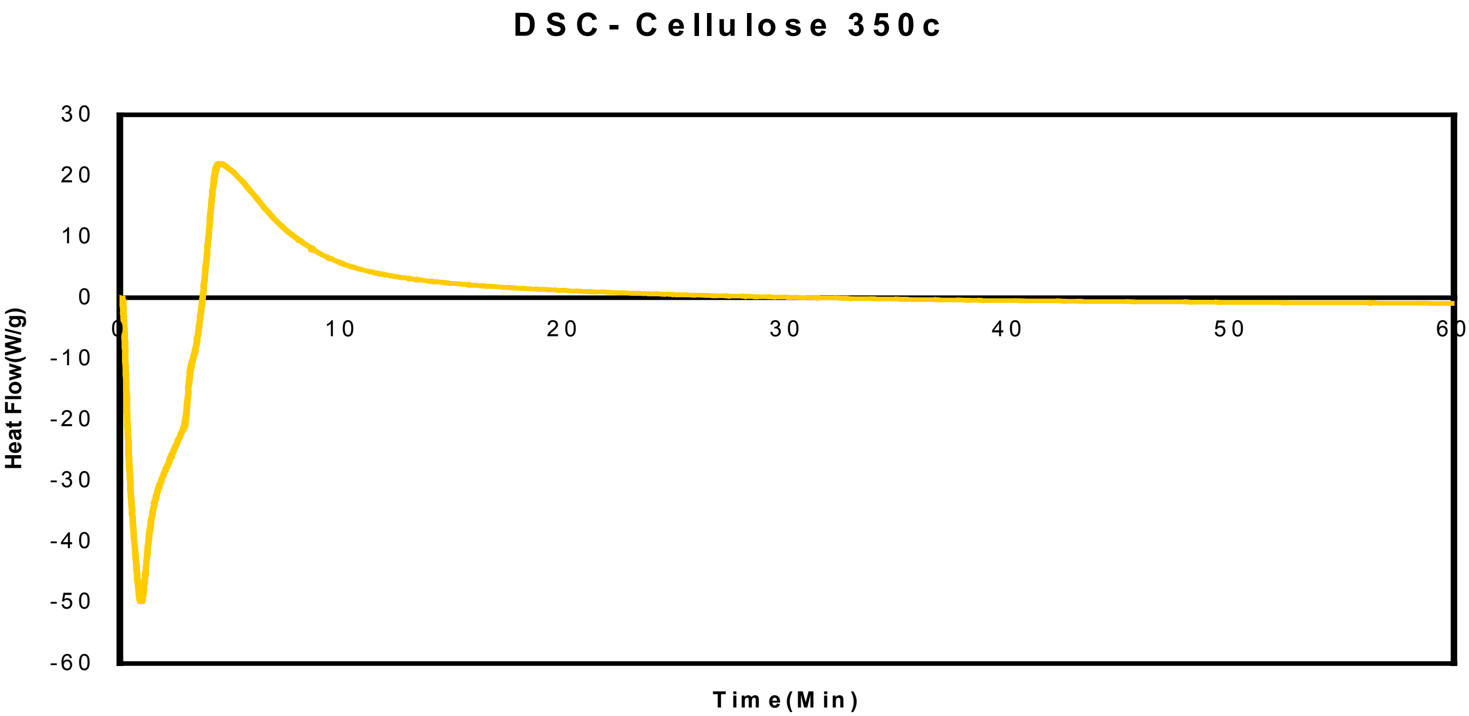

DSC - Cellulose 350c
Heat Flow(W/g)
Time(Min)
30
20
10
0
-10
-20
-30
-40
-50
-60
0
10
20
30
40
50
60

Figure 4:

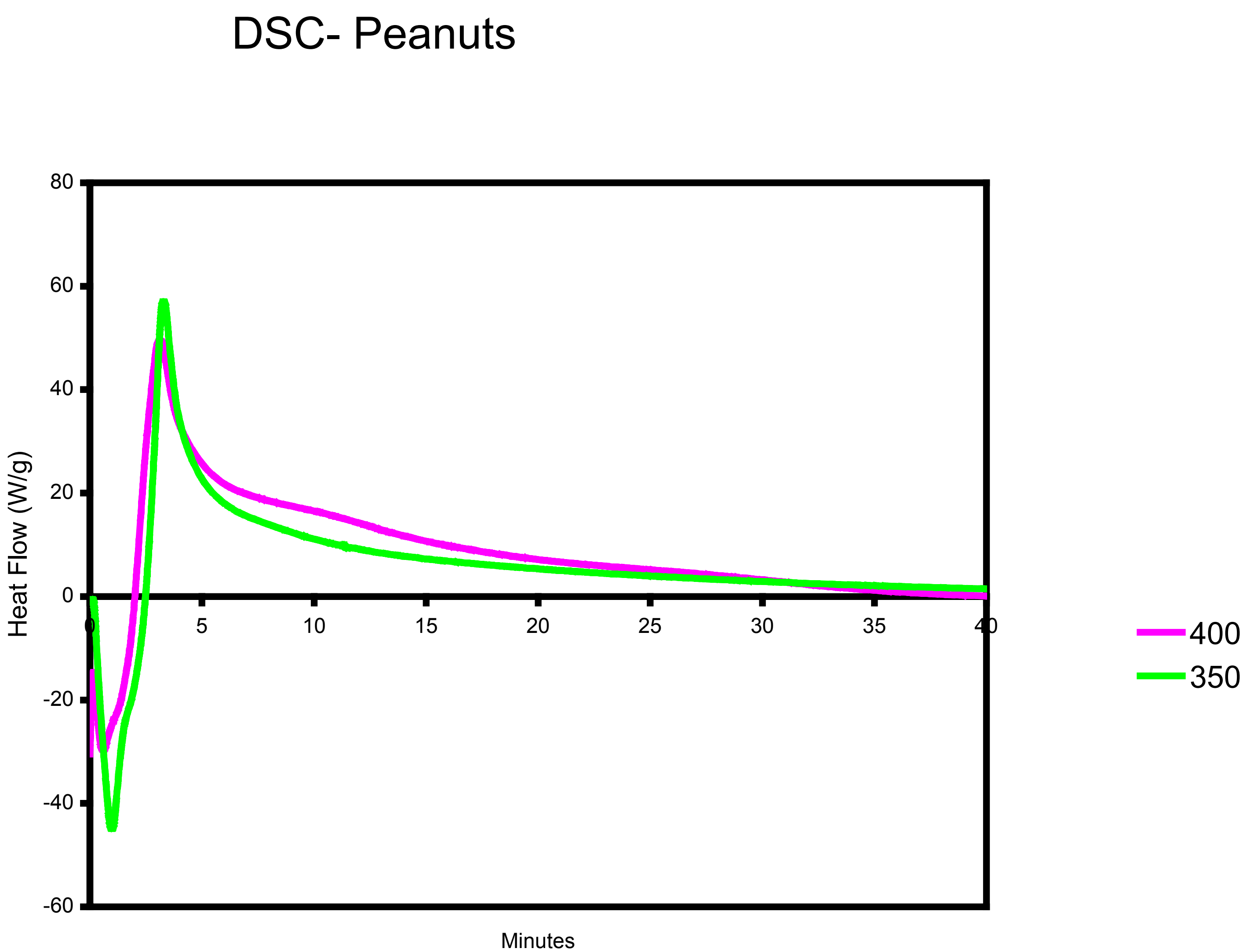
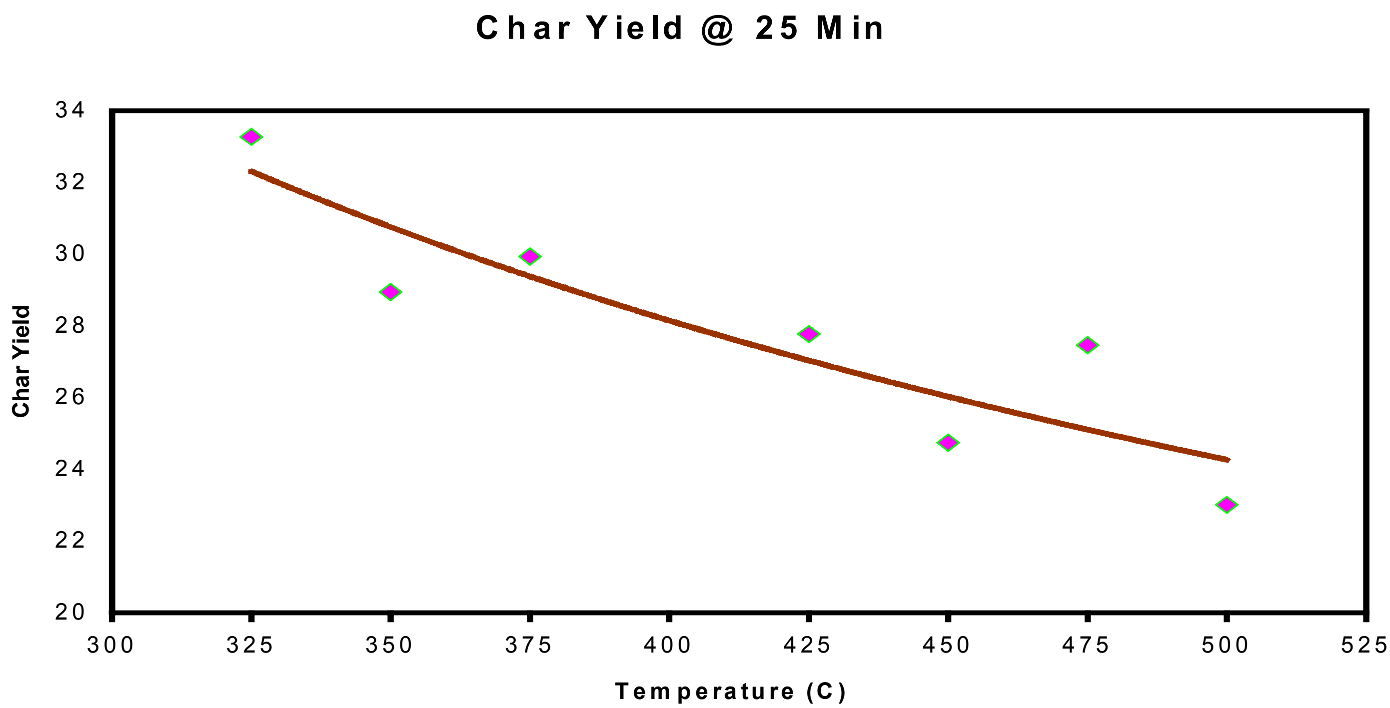

DSC- Peanuts
Heat Flow (W/g)
80
60
40
20
0
-20
-40
-60
0
5
10
15
20
25
30
35
40
Minutes
400
350

Figure 5:


Char Yield @ 25 Min
34
32
30
28
26
24
22
20
Char Yield
300
325
350
375
400
425
450
475
500
525
Temperature (C)