

**EFFECT OF USING INERT AND NON-INERT GASES ON THE
THERMAL DEGRADATION AND FUEL PROPERTIES OF BIOMASS IN
THE TORREFACTION AND PYROLYSIS REGION**

A Thesis

by

DUSTIN E. ESELTINE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Mechanical Engineering

Effect of Using Inert and Non-Inert Gases on the Thermal Degradation and Fuel Properties of

Biomass in the Torrefaction and Pyrolysis Region

Copyright 2011 Dustin E. Eseltine

**EFFECT OF USING INERT AND NON-INERT GASES ON THE
THERMAL DEGRADATION AND FUEL PROPERTIES OF BIOMASS IN
THE TORREFACTION AND PYROLYSIS REGION**

A Thesis

by

DUSTIN E. ESELTINE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Co-Chairs of Committee, Kalyan Annamalai
Devesh Ranjan
Committee Members, Timothy Jacobos
Sergio Capareda
James Ansley

Head of Department, Jerald Caton

December 2011

Major Subject: Mechanical Engineering

ABSTRACT

Effect of Using Inert and Non-Inert Gases on the Thermal Degradation and Fuel Properties of Biomass in the Torrefaction and Pyrolysis Region.

(December 2011)

Dustin E. Eseltine, B.S. ,Wentworth Institute of Technology

Co-Chairs of Advisory Committee, Dr. Kalyan Annamalai
Dr. Devesh Ranjan

The research presented focuses on the use of Carbon-dioxide (CO₂), Nitrogen (N₂) and Argon (Ar) as purge gases for torrefaction. Torrefaction using CO₂ as a purge gas may further improve the fuel characteristics of the torrefied fuel when compared to N₂ and Ar (which are entirely inert), making it better suited for use as a fuel for co-firing with coal or gasification. Three different biomasses were investigated: Juniper wood chips, Mesquite wood chips, and forage Sorghum.

Experiments were conducted using a thermo-gravimetric analyzer (TGA, TA Instruments Model Q-600) to determine the effect of the purge gas over a wide range of torrefaction temperatures (200-300°C). TGA weight traces (thermograms) showed an increased mass loss when using CO₂ as a purge gas when compared to N₂. The increased mass loss when CO₂ was used is attributed to a hypothesized reaction between the CO₂ and fixed Carbon contained within the biomass. Torrefaction of biomass, using Ar as the purge gas, produced results similar to torrefaction using N₂. Derivative Thermo-Gravimetric analysis (DTG) was done to determine the temperature ranges over which the three main components of biomass (hemicellulose, cellulose, and lignin) decomposed. The DTG results are in agreement with previously published research. From TGA thermograms and DTG analysis it was determined that torrefaction at higher temperatures (>260°C) likely result in the breakdown of cellulose during torrefaction, an undesired outcome.

Proximate, ultimate, and heat value analysis was done on all three biomasses. All three contain a relatively high Oxygen content, which serves to decrease the higher heating value (HHV) of the biomass. The HHV of Juniper, Mesquite, and Sorghum on a dry ash-free (DAF) basis were

20,584 kJ/kg, 20,128 kJ/kg, and 19,389 kJ/kg respectively. The HHV of the three biomasses were relatively constant as expected for agricultural biomass.

From TGA analysis (thermograms and DTG), an optimal torrefaction temperature was determined (240°C) based upon the amount of mass lost during torrefaction and estimates of energy retained. Batch torrefaction of all three biomasses at the optimal torrefaction temperature was completed using a laboratory oven. All three biomasses were torrefied using CO₂, N₂, and Ar as a purge gas. Proximate, ultimate, and heat value analysis was done for each of the torrefied fuels and compared. Results of the fuel property analysis showed torrefaction reduced the moisture content and oxygen percentage of the fuel resulting in the torrefied biomass having a larger HHV when compared to raw biomass. Due to inherent mass lost during torrefaction, the amount of energy retained in the torrefied biomass was calculated to determine the percentage of the virgin biomass energy content that remained. Torrefaction using CO₂ resulted in the lowest amount of energy retention of all three purge gases tested (78.86% for Juniper); conversely, Nitrogen resulted in the highest amount of energy retention (91.81% for Sorghum.) Torrefaction of the biomass also increased the fixed carbon (FC) content of the fuel.

The grindability of the torrefied biomass was investigated via size distribution analysis of the raw and ground biomass. Initial size distribution analysis showed that torrefaction of Mesquite and Juniper resulted in smaller particle sizes; with a greater fraction of the torrefied biomass passing through smaller meshes. Analysis of the ground biomass samples showed that torrefaction improved the grindability of the fuel. The percent of torrefied biomass that passed through an 840µm mesh increased by over 20% for both Mesquite and Juniper when ground. Sorghum exhibited similar increases; however, the amount of increase is less apparent due to the smaller particle size distribution of the raw Sorghum.

DEDICATION

To my family and friends who have helped me in this endeavor. Without your patience, guidance, and understanding this surely would not have been possible.

ACKNOWLEDGMENTS

I would like to start by thanking Dr. Kaylan Annamalai, the chair of my advisory committee, for his support throughout this process. The time you have given me is invaluable, and I greatly appreciate all of your guidance. It has been a pleasure to work and learn with you. I would like to thank Dr. Devesh Ranjan, the co-chair of my advisory committee, for his support and interest in my research. Both yours and Dr. Annamalai's interest in this research has fueled my own interest and allowed me to thoroughly enjoy the time I have spent on it. I would also like to thank Dr. Timothy Jacobs for serving on my committee. I would also like to thank him for introducing me to the wonderful world of combustion, a subject I find myself thoroughly entranced by. I would like to thank Dr. Jim Ansley for serving on my committee, as well as providing the raw fuel used for analysis. I would also like to thank Dr. Sergio Capareda for taking time out of his busy schedule to serve on my committee.

A special thanks also goes out to my colleagues at the Coal and Biomass Energy Lab (CABEL) at Texas A&M: Ben Lawrence, Siva Sankar Thanapal, Aubrey Spear, and Wei Chen. It was a pleasure working with you all. Your insight has been invaluable, especially Ben Lawrence's, whose advice has continually pushed me in the right direction.

I would like to thank my parents. First, my mother, Roberta Hier, for her patience and understanding while I undertook this endeavor. You have taught me much and always provided me with a voice of reason whenever I might waiver. I would like to thank my father Nathan Eseltine for pushing me to pursue what has become one of the best undertakings in my life. Your support has allowed me to achieve such lofty heights. I would also like to thank Terry Hier for pushing me to pursue constantly whatever it is that makes me happy. I would like to thank Geoff Eseltine for being the best friend, mentor, and brother one could ask for. Finally, I would like to thank the beautiful and loving Jocelyn Martin. Your love and support over the past few years have given me the strength to continue to strive for excellence in my life. I love you all so very much, and hope I have made you proud.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
DEDICATION	v
ACKNOWLEDGMENTS	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES	ix
LIST OF TABLES	xi
NOMENCLATURE	xiii
1. INTRODUCTION	1
2. LITERATURE REVIEW AND SCOPE OF WORK	5
3. EXPERIMENTAL TORREFACTION STUDY	13
3.1 Experiential Facility	13
3.1.1 ThermoGravimetric Analyzer.....	13
3.1.2 Laboratory Oven.....	14
3.2 Experimental Procedure	15
3.2.1 Sample Preparation.....	15
3.2.2 Thermogravimetric Analysis	15
3.2.3 Torrefied Fuel Properties.....	19
3.2.4 Grindability Analysis.....	19
3.2.5 Hydrophobicity Test.....	20
3.3 Data Analysis.....	20
3.3.1 TGA Thermograms.....	20
3.3.2 DTG Analysis.....	22
4. RESULTS AND DISCUSSION	24
4.1 Introduction	24
4.2 Raw Biomass Fuel Properties.....	24
4.3 TGA.....	27
4.3.1 Mesquite	27
4.3.2 Juniper	33
4.3.3 Sorghum	39
4.4 DTG Analysis.....	46
4.4.1 Mesquite	46
4.4.2 Juniper	50
4.4.3 Sorghum	54
4.5 TGA/DTG Discussion and Hypotheses.....	59
4.6 Determination of Optimal Torrefaction Temperature	62
4.7 Torrefaction Using a Laboratory Oven.....	64
4.8 Grindability Analysis.....	70
4.9 Hydrophobicity.....	74

	Page
5. CONCLUSIONS AND FUTURE STUDIES	76
6. REFERENCES.....	78
APPENDIX A: PRINCIPLES OF TGA OPERATION.....	81
APPENDIX B: RAW AND TORREFIED BIOMASS FUEL PROPERTIES	83
APPENDIX C: PRELIMINARY CARBON-DIOXIDE RESIDENCE TIME STUDIES.....	91
VITA	94

LIST OF FIGURES

	Page
Fig. 1.1- World energy use by fuel type. [1]	1
Fig. 1.2 - Worldwide CO ₂ emissions from energy consumption sorted by fuel source. [1]	3
Fig. 2.1 - Percent energy generation by source for the year 2010 [4]	5
Fig. 2.2 – The effect of the O/C ratio and H/C ratio on the HHV of a fuel. [7]	6
Fig. 3.1 - Schematic of the TGA setup used during experimentation (Adapted from [23])	13
Fig. 3.2 – Schematic of the laboratory oven setup used to torrefy raw biomass.	14
Fig. 3.3 – The TGA beams with empty reference and test pans.....	16
Fig. 3.4 – Sample thermogram from the pyrolysis of lignocellulosic biomass.	21
Fig. 3.5 – Sample DTG chart of lignocellulosic biomass.....	22
Fig. 3.6 – Sample TGA/DTG chart for lignocellulosic biomass.	23
Fig. 4.1 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using N ₂ as the purge gas.	28
Fig. 4.2 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using Ar as the purge gas.	29
Fig. 4.3 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using CO ₂ as the purge gas.	30
Fig. 4.4 - Comparison of thermograms from pyrolysis and torrefaction of Mesquite wood using N ₂ and Ar as the purge gases.....	31
Fig. 4.5- Comparison of thermograms from pyrolysis and torrefaction of Mesquite wood using N ₂ and CO ₂ as the purge gases.	32
Fig. 4.6 - TGA thermograms of Juniper wood pyrolysis and torrefaction using N ₂ as the purge gas.	34
Fig. 4.7 - TGA thermograms of Juniper wood pyrolysis and torrefaction using Ar as the purge gas.	35
Fig. 4.8 - TGA thermograms of Juniper wood pyrolysis and torrefaction using CO ₂ as the purge gas.	36
Fig. 4.9 - Comparison of thermograms from pyrolysis and torrefaction of Juniper wood using N ₂ and Ar as the purge gasses.	37
Fig. 4.10 - Comparison of thermograms from pyrolysis and torrefaction of Juniper wood using N ₂ and CO ₂ as the purge gases.	38
Fig. 4.11 - TGA thermograms of Sorghum pyrolysis and torrefaction using N ₂ as the purge gas.	41

	Page
Fig. 4.12 - TGA thermograms of Sorghum pyrolysis and torrefaction using Ar as the purge gas.....	42
Fig. 4.13 - TGA thermograms of Sorghum pyrolysis and torrefaction using CO ₂ as the purge gas.....	43
Fig. 4.14 - Comparison of thermograms from pyrolysis and torrefaction of Sorghum using N ₂ and Ar as the purge gas.....	44
Fig. 4.15 - Comparison of thermograms from pyrolysis and torrefaction of Sorghum using N ₂ and CO ₂ as the purge gas.....	45
Fig. 4.16- DTG distribution of Mesquite wood pyrolysis and torrefaction using N ₂ as the purge gas.....	47
Fig. 4.17 – DTG distribution of Mesquite wood pyrolysis and torrefaction using Ar as the purge gas.....	48
Fig. 4.18 – DTG distribution of Mesquite wood pyrolysis and torrefaction using CO ₂ as the purge gas.....	49
Fig. 4.19 – DTG distribution of Juniper wood pyrolysis and torrefaction using N ₂ as the purge gas.....	51
Fig. 4.20 – DTG distribution of Juniper wood pyrolysis and torrefaction using Ar as the purge gas.....	52
Fig. 4.21 – DTG distribution of Juniper wood pyrolysis and torrefaction using CO ₂ as the purge gas.....	53
Fig. 4.22 - DTG distribution of Sorghum pyrolysis and torrefaction using N ₂ as the purge gas.....	56
Fig. 4.23 - DTG distribution of Sorghum pyrolysis and torrefaction using Ar as the purge gas.....	57
Fig. 4.24 - DTG distribution of Sorghum pyrolysis and torrefaction using CO ₂ as the purge gas.....	58
Fig. 4.25 – Specific heat values of the purge gases used during experimentation over a wide temperature range.....	60
Fig. 4.26 - The Boudouard reaction over a wide temperature range. [24].....	61
Fig. A.0.1 – TA Q600 beam and counter weight setup.....	81
Fig. C.0.1 – The effect of residence time on the torrefaction of biomass in a Carbon-dioxide environment.....	92

LIST OF TABLES

	Page
Table 4.1 – Proximate, ultimate, and heat value analysis of the raw biomass used for experimentation (reported on an as received basis unless otherwise noted.).....	25
Table 4.2 – Proximate, ultimate, and heat value analysis of Texas Lignite (TXL) and Powder River Basin (PRB) coal (reported on an as received basis unless otherwise noted). [13].....	26
Table 4.3 – Average heater power required to maintain 240°C temperature during the torrefaction of juniper wood.	62
Table 4.4 – Estimated energy retained for all three biomass and purge gases for the entire range of torrefaction temperatures.	64
Table 4.5 – Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Nitrogen as the purge gas (reported on an as received basis unless otherwise noted).....	66
Table 4.6 – Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Argon as the purge gas (reported on an as received basis unless otherwise noted).....	67
Table 4.7 - Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Carbon-dioxide as the purge gas (reported on an as received basis unless otherwise noted).....	68
Table 4.8 – Calculated values of percent energy retained for torrefied biomass.....	69
Table 4.9 – Size distribution analysis for un-ground virgin and torrefied biomass.....	72
Table 4.10 - Size distribution analysis for ground virgin and torrefied biomass.....	73
Table 4.11 – Results of hydrophobicity tests conducted on raw and torrefied biomass.	75
Table B.1 – Raw biomass fuel properties on a dry basis.....	83
Table B.2 –Fuel properties of biomass torrefied in a Nitrogen environment presented on a dry basis.	84
Table B.3 – Fuel properties of biomass torrefied in a Argon environment presented on a dry basis.	85
Table B.4 – Fuel properties of biomass torrefied in a Carbon-dioxide environment presented on a dry basis.	86
Table B.5 – Raw biomass fuel properties on a dry ash free basis.	87
Table B.6 – Fuel properties of biomass torrefied in a Nitrogen environment presented on a dry ash free basis.....	88
Table B.7 – Fuel properties of biomass torrefied in an Argon environment presented on a dry ash free basis.....	89

	Page
Table B.8– Fuel properties of biomass torrefied in a Carbon-dioxide environment presented on a dry ash free basis.....	90
Table C.1 – Estimate energy retention for mesquite torrefied in a Carbon-dioxide environment at varying residence times.	93

NOMENCLATURE

AR	As Received
DAF	Dry Ash-Free
DTG	Derivative Thermo-Gravimetric
FC	Fixed Carbon
HHV	Higher Heating Value
HVY	Heating Value Yield
LHV	Lower Heating Value
\dot{m}	Mass Flow Rate
mg	Milligram
ml	Milliliter
mm	Millimeter
μm	Micrometer
O/C	Oxygen-Carbon Ratio
O.D.	Outside Diameter
PSI	Pounds per Square Inch
RB	Raw Biomass
SCFH	Standard Cubic Feet per Hour
SG	Specific Gravity
TGA	Thermo-Gravimetric Analysis/Analyzer
TB	Torrefied Biomass
VM	Volatile Matter

Subscripts

RB	Raw Biomass
TB	Torrefied Biomass

1. INTRODUCTION

With the continued increase in fossil fuel consumption worldwide (Fig. 1.1) [1], and concerns surrounding the depletion of natural resources, research in recent years has focused on improving energy usage (via efficiency, co-combustion, etc.) and renewable energy.

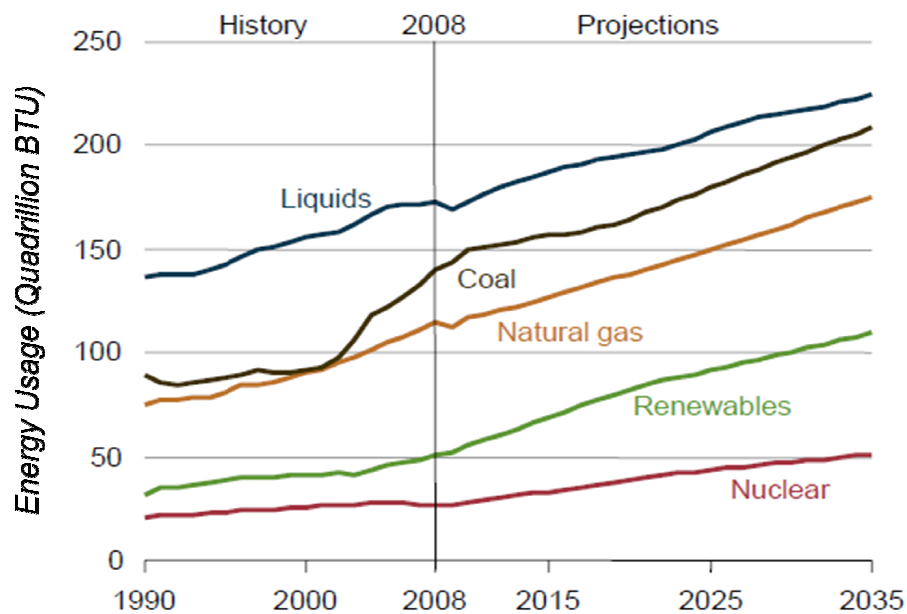


Fig. 1.1- World energy use by fuel type. [1]

Torrefaction, an area of renewable energy research that has seen a significant growth over the last decade, is a process that aims to increase the energy content of a biomass by heating the biomass for a given period of time (residence time) in the absence of oxygen at a constant temperature (residence temperature) between 200-300°C .

This thesis follows the style of Fuel.

In this temperature range the biomass loses a significant amount of its original moisture content and low weight volatiles are released that contain high amount of Oxygen and Hydrogen. The torrefaction process therefore results in a decrease in the Oxygen to Carbon ratio (O/C) effectively increasing the energy content of the biomass.

Apart from the higher energy content, the torrefied biomass has several other benefits. Biomass subjected to torrefaction becomes brittle, requiring less energy to grind. This makes torrefied biomass easy to pulverize and co-fire with coal. A higher energy biomass is also desirable from a transportation standpoint. The brittle biomass weighs less and has higher energy content when compared to virgin biomass, allowing for more biomass with higher energy content to be transported for the same cost as transporting virgin biomass. Biomass that has been torrefied also exhibits hydrophobic qualities allowing for easier storage, the biomass can be stored for long periods of time and used without having to undergo some type pre-treatment process to dry the fuel before use.

One outcome of the continued use of coal and other fossil fuels is the persistent production of Carbon-dioxide (Fig.1.2), a harmful emission of combustion. Recent studies funded by the U.S. Department of Energy have focused on CO₂ sequestration [2] as one of the uses for CO₂ produced from coal fired power plants among other things.

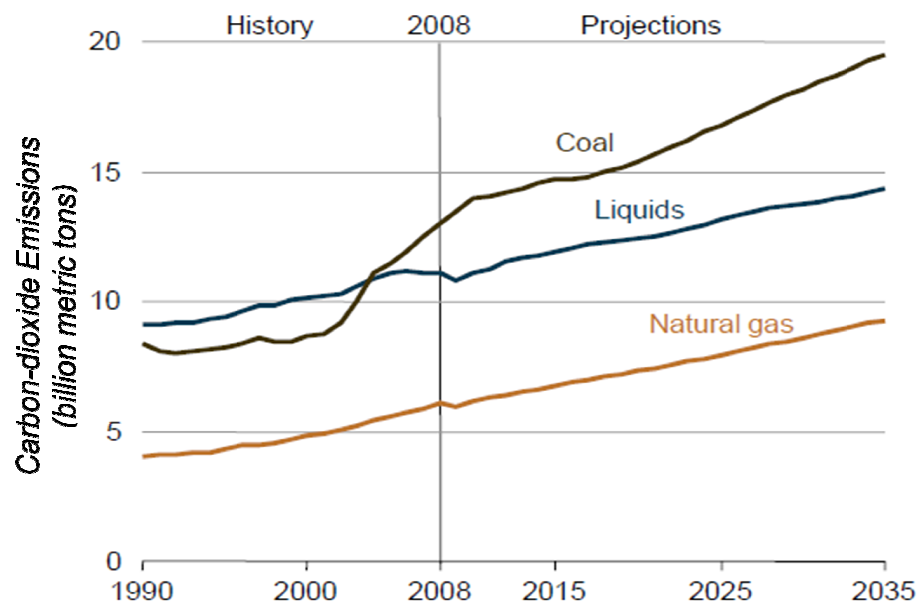


Fig.1.2 - Worldwide CO₂ emissions from energy consumption sorted by fuel source. [1]

Biomass is a source of energy that is considered to be Carbon neutral. Any Carbon-dioxide released from the thermal conversion of biomass is considered to part of the natural carbon cycle [3] as plants absorb Carbon-dioxide via photosynthesis. Therefore, increasing the amount of biomass used to produce usable energy will further decrease the impact Carbon-dioxide emissions currently have on the environment. Furthermore, using Carbon-dioxide to thermally upgrade the fuel is an intriguing possibility as the CO₂ is produced from combustion and gasification could be recycled to further improve the fuel properties of the biomass being used.

With these factors in mind, this research focused on analyzing the effect of utilizing CO₂ as a purge gas medium for the torrefaction of three biomasses commonly found in Texas (Juniper wood, Mesquite wood, and Sorghum.) The effect of the purge gas was evaluated by determining the weight loss from torrefaction. Each of the three biomasses was torrefied between 200°C to 300°C in 20°C increments using a TGA. Weight loss curves were obtained from the TGA and the results using CO₂, N₂, and Ar as the purge gases were compared. Given that previous studies have used Nitrogen as the torrefaction medium, Nitrogen was used as the base line purge gas. Argon was used as a purge gas to potentially rule out different thermo-chemical properties of the gases as a cause for trends that may occur. The data obtained from TGA was also used to complete DTG analysis and determine how the hemicelluloses, cellulose, and lignin fractions of

each biomass thermally degraded. The DTG analysis was integral in determining the optimal torrefaction temperature, this being the temperature that would result in the maximum break down of hemicelluloses with minimal breakdown of the cellulose structure in the biomass. The biomass was also pyrolyzed, a process where the fuel is heated at a constant rate in an inert environment. Pyrolysis was completed using the TGA and with CO₂, N₂, Ar as purge gases. The pyrolysis weight traces were used as base-line curves to determine the overall effect torrefaction had upon the breakdown of the hemicellulose, cellulose, and lignin.

Further tests were done using a laboratory oven to torrefy the biomass. These tests were conducted at a single torrefaction temperature (240°C) determined from TGA/DTG analysis and previous research in literature. As with the TGA studies, three different purge gases were used for torrefaction in the laboratory oven, CO₂, N₂, and Ar. Proximate, ultimate, and heat value analysis was done on the biomass torrefied in the laboratory oven, and the results were compared to see if any differences in fuel properties occurred as a result of using different purge gases. The biomass torrefied in the laboratory oven were also subjected to grindability tests as well as hydrophobicity testing to further investigate the effect torrefaction with different purge gases had upon characteristics of the biomass.

From the results presented, conclusions can be made regarding the optimal torrefaction temperature as well as the effect of purge gas upon torrefied biomass. Finally, future research is proposed based upon the presented results.

2. LITERATURE REVIEW AND SCOPE OF WORK

Currently coal is used to provide roughly 45% of the electricity used in the United States [4], with renewable energy sources (such as biomass) providing only 5.5% (Fig. 2.1). The harmful emissions produced from coal combustion have driven research into the development of renewable energy sources. Although biomass has been extensively studied as a renewable energy source, most research conducted uses raw untreated biomass.

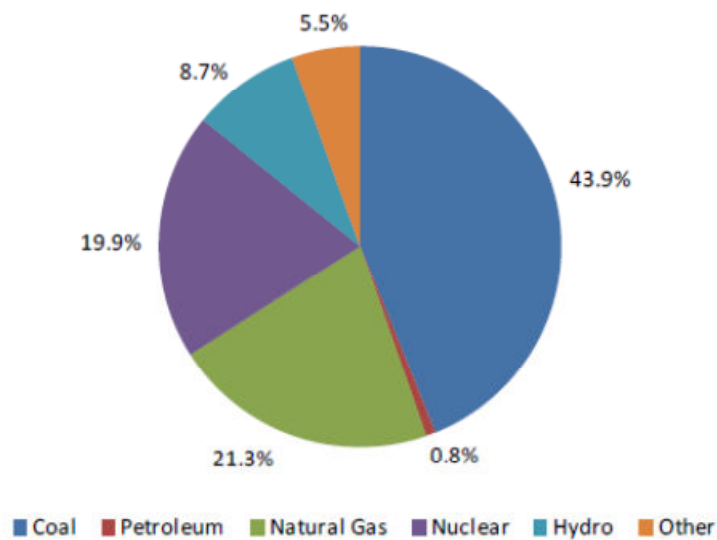


Fig. 2.1 - Percent energy generation by source for the year 2010 [4]

Recent studies using biomass as a gasification fuel [5] as well as using biomass in co-firing applications [6] has shown promising results. While the use of raw biomass as a renewable energy source has potential, pretreatment of raw biomass could further enhance its capabilities as a fuel. Raw biomasses have relatively low energy contents and generally contain high amounts of moisture resulting in reduced conversion efficiency. The higher amount of oxygen contained within biomass also results in a lower calorific value. The Boie equation is a method of calculating the HHV of a fuel based upon the fraction of Carbon, Oxygen, Hydrogen, Nitrogen, and Sulfur contained within the fuel [7]:

$$HHV \left(\frac{kJ}{Kg} \right) = 35,160Y_C + 116,225Y_H - 11,090Y_O + 6,280Y_N + 10,465Y_S \quad (1)$$

As seen in the above equation the only elemental fraction with a negative coefficient is Oxygen, therefore the higher the Oxygen content of a fuel the smaller the HHV. Furthermore, the ratio of Oxygen to Carbon in a fuel will directly affect the fuels HHV (Fig. 2.2).

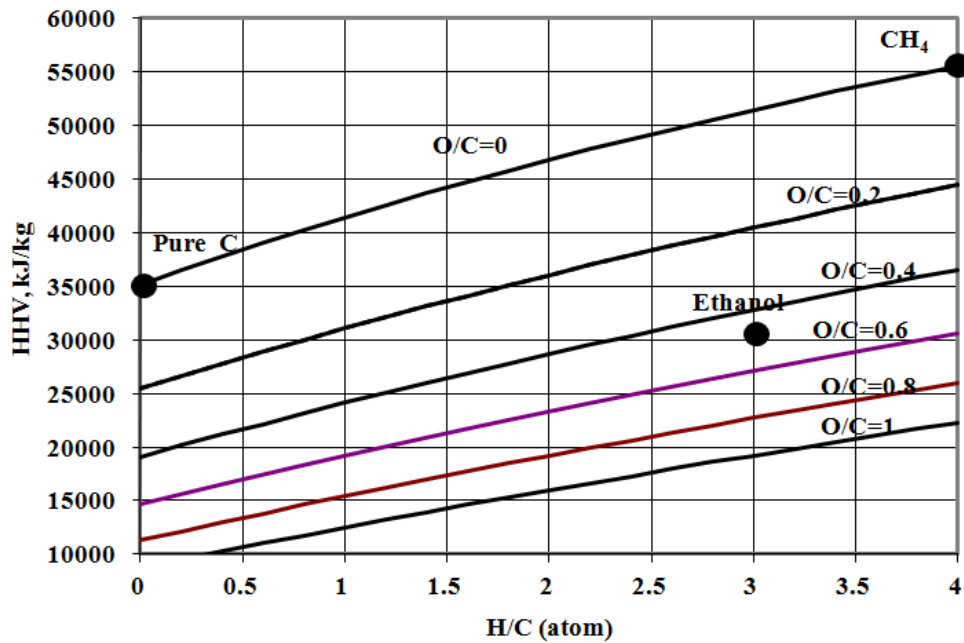


Fig. 2.2 – The effect of the O/C ratio and H/C ratio on the HHV of a fuel. [7]

The torrefaction process directly affects the Oxygen content via the liberation of volatiles that contain Oxygen. This causes a decrease in the O/C ratio and results in a biomass with a larger HHV.

Torrefaction is a pretreatment process that aims to improve the quality of biomass by reducing the moisture content and increasing its calorific value via decreasing the oxygen percentage within the biomass. This is done by heating biomass at a constant temperature between 200-300°C for a set period of time in an inert environment. Under certain torrefaction conditions the resulting biomass can have properties comparable to low rank coals [8]. Increasing the calorific

content of biomass by lowering the oxygen-carbon ratio makes it more suitable for use as a fuel for gasification [9]. This coupled with the increased grindability makes torrefied biomass an attractive fuel for co-firing applications as well.

Research done by Arias *et al.* [3] on the torrefaction of eucalyptus showed that torrefaction of raw biomass increases the grindability of the biomass. Eucalyptus samples were torrefied between 240°C and 280°C with varying residence times between 15 minutes to 3 hours. Size distribution analysis of the samples showed an increase in the residence time at a given temperature resulted in smaller particle sizes, indicating easier grindability. Chen *et al.* [10] indicated lower torrefaction temperatures had a slight effect on the grindability of the fuel, though an increase in residence time at lower temperatures had no effect. At temperatures greater than 250°C the grindability of the biomass can be greatly improved at longer residence times (>1h). Similar studies conducted by Phanphanich *et al.* [11] determined that the energy required to grind the torrefied biomass can be reduced up to ten times compared to the energy required to grind raw biomass.

During torrefaction the inherent mass loss results in a loss of energy when compared to the original mass of the sample. In order to determine the amount of energy retained, the heating value yield must be calculated. Further analysis of the results of Arias *et al.* [3] show that increasing residence temperature has a much greater effect on heating value yield than increasing the residence time. The eucalyptus samples torrefied at 240°C (mild torrefaction) for 30 minutes had a 90% heating value yield where as the sample torrefied at 280°C (severe torrefaction) for the same residence time had a 60% heating value yield. These results are in good agreement with other studies by Chen and Kuo [7] and Bridgeman [12]. Furthermore it was determined that a severe torrefaction temperature of 280°C resulted in a 40% increase in the HHV of woody biomass, however, over 50% of the initial weight was lost from the torrefaction process [10]. Results of studies by Bridgeman *et al.* [13] on the torrefaction of wheat straw, reed canary grass, and willow coppice produced similar results. As torrefaction temperature increased there was a marked decrease in both mass yield and energy yield.

Residence time has also been shown to directly affects the moisture, volatile matter (VM), fixed carbon (FC), and ash content in the torrefied fuel [3]. Increasing residence time results in a decrease in the amount of moisture in the torrefied biomass. However, this also results in a decrease in VM as well as a very minimal increase in ash content. The change in fuel properties

has been found to be effected by both residence time and residence temperature. Several other studies such as those done by Prins *et al.* [14] and others [12,13] show similar results with the overall consensus being that the change in fuel properties is more dependent upon residence temperature rather than residence time. Although higher torrefaction temperatures produce a fuel with a higher energy density than that of raw biomass, a compromise between mass loss and energy density must be utilized in order to produce the most optimal fuel from torrefaction.

Other research by Bridgeman *et al.* [12] further noted that increasing torrefaction temperatures also resulted in a significant change in the elemental composition of biomass. Ultimate analysis illustrated a decrease in the Oxygen-Carbon ratio of the torrefied biomass, the change in the Oxygen-Carbon ratio becoming more significant as residence temperature increases. Studies done by Prins *et al.* [14] on the torrefaction of wood show that the amount of change in the Oxygen-Carbon ratio is related to the type of biomass, with beech and willow (deciduous wood) having a larger decrease than that of larch (coniferous wood). It has also been shown the fuel properties of herbaceous biomass tend to change more than the properties of woody biomass [13]. Furthermore, different amounts of mass loss between different biomasses torrefied under the same conditions has been observed. The variation in mass loss has been mainly attributed to the different chemical composition between biomasses tested. Hemicellulose, cellulose, and lignin are the main constituents that comprise the cell structure of lignocellulosic biomass. Changes in the percent of each constituent causes variation in the results obtained from the torrefaction of different biomasses. Prins *et al.* [15] has described the composition of the cellular structure as “On a microscopic scale, wood cell walls are composed of so-called microfibrils, bundles of cellulose molecules ‘coated’ with hemicellulose. In between the microfibrils...lignin is deposited.”

Chemical composition and the thermal degradation of various biomasses is an important factor in understanding the torrefaction process. Recently there has been a significant amount of research done on how the composition of lignocellulosic biomass the thermally degrades. Chen and Kuo [8,16] have completed studies on the effect of torrefaction temperature on the lignocellulosic structure of several different biomass. One study by Chen and Kuo[8] focused on the torrefaction of bamboo, willow, coconut shell and ficus wood. Torrefaction of the biomass was carried out using a TGA/DTA with Nitrogen as a purge gas at a fixed flow rate. The samples were heated from ambient conditions to two torrefaction temperatures (240°C, 275°C), torrefied

for two hours, and then heated to 800°C. A comparison of the DTG curves of pyrolyzed biomass to those undergoing torrefaction showed that a mild torrefaction temperature (240°C) had a significant effect on the breakdown of hemicellulose while having a minimal impact on lignin and cellulose. Torrefaction at a high temperature (275°C) resulted in further breakdown of the lignin and cellulose resulting in a significant mass loss in the torrefied biomass. TGA weight trace curves showed a chemically frozen zone immediately following the torrefaction process, indicating that the reaction intensity is greatest during the initial stage of torrefaction.

The breakdown of the lignocellulosic structure of torrefied biomass has also been investigated further by Chen *et al.* [10]. DTG analysis comparing raw biomass to torrefied biomass gives more insight into the effect of torrefaction upon the lignocellulosic structure. Results from the torrefaction of Lauan wood show that, when compared to raw biomass, light torrefaction (220°C) causes hemicellulose to breakdown with no marked effect upon cellulose or lignin. Results from mild (250°C) and severe torrefaction (280°C) are comparable to previous studies by Chen and Kuo[8].

Further research [16] has focused on the torrefaction of the basic constituents of biomass. Five different samples that comprise the basic constituents of lignocellulosic biomass were tested, hemicellulose, cellulose, lignin, xylan (a component of hemicelluloses) and dextran. The samples were torrefied individually and a blend of hemicellulose, cellulose, and lignin was torrefied as well. Torrefaction was carried out using the same method as previous research[8] with three different residence temperatures meant to represent a light (230°C), mild (260°C), and severe (290°C) torrefaction. The TGA weight traces of the hemicellulose, cellulose, and lignin samples showed that the light torrefaction process had a minimal effect on the breakdown of the samples. However, the mild torrefaction temperature (260°C) showed a significant increase in the weight loss of hemicellulose occurred. The effect of mild torrefaction on lignin and cellulose remained the same with less than 5.0% weight loss for either. When the three samples were subjected to heavy torrefaction there was a significant impact on the mass loss in both cellulose and hemicellulose, while there was little increase in the mass loss of lignin compared to mild torrefaction. Overall it was determined that a light torrefaction process only serves to remove moisture and light volatiles, while mild and severe torrefaction results in drastic degradation of hemicellulose with a significant breakdown of cellulose occurring during severe torrefaction. These results coupled with other literature [3,8,14] indicate that severe torrefaction (>275°C) of

biomass produces undesired results. Furthermore the co-torrefaction of a hemicellulose, cellulose, lignin blend showed no interaction between the three constituents. Light torrefaction of the blend resulted in a small weight loss with weight loss due to mild torrefaction being mostly dependent upon the hemicellulose fraction. The DTG curve from mild torrefaction resulted in the pyrolysis peak of hemicellulose disappearing, indicating that a majority of the hemicellulose had broken down during the initial torrefaction process. After severe torrefaction the pyrolysis peak of cellulose showed a marked decrease indicating that severe torrefaction had a significant impact on the breakdown of cellulose. Co-torrefaction showed no interaction between the three constituents (hemicellulose, cellulose, and lignin) and it was determined that the weight loss of biomass could be predicted fairly well from the weight loss of each of the individual constituents. Further studies by Raveendran *et al.* [17] also concluded that the composition has a more significant impact upon the combustion properties of biomass than the interaction between constituents.

The effect torrefaction has upon the three main constituents is of particular interest due to the chemical makeup of hemicellulose, cellulose, and lignin. Understanding the chemical behavior of these components is integral in optimizing the torrefaction process. Demirbaş [18] investigated the percent of each of the three main constituents of lignocellulosic biomass and their contribution to the HHV of the fuel. Seven different biomass were used and the percent of hemicellulose, cellulose, and lignin in each biomass was determined using ASTM standards [19]. The ASTM standards used were withdrawn in 1985; however, they still provide the best standard for elemental and structural analyses today. From the analysis of the structural composition it was determined that, in general, an increase in the amount lignin in a lignocellulosic biomass results in an increase in HHV. Elemental composition analysis of the lignin portion of each biomass indicated that lignin has an increased Carbon content and decreased Oxygen content when compared to hemicellulose and cellulose. This decrease in the O/C ratio between lignin and the other two constituents (hemicellulose and cellulose) is what causes lignin to have a higher HHV. Based upon the data obtained it was determined that there is no direct relation between the hemicellulose and cellulose content of a biomass and its HHV. However, there is a good relation between the amount of lignin within a biomass and the HHV of the biomass. The importance of lignin becomes magnified in torrefied biomass due to most research [3,8,14] suggesting a mild torrefaction process (240-250°C) for the pretreatment of biomass. Mild torrefaction, which causes a significant breakdown in hemicellulose, a moderate

breakdown in cellulose, leaves lignin as the main contributor to the HHV of the resulting biomass.

The thermal breakdown of the lignocellulosic components of biomass was further studied by Yi-min *et al.* [20] using a TGA. Three different compounds were used to model the three major components of biomass: xylan (a major component of hemicellulose), avicel (cellulose), and alkali lignin. Ultimate analysis of the three substances showed similar results compared to other literature [18], with lignin having a lower oxygen-carbon ratio than cellulose and hemicellulose. Weight trace curves and DTG analysis of the data clearly showed the thermal breakdown of each component. The majority of hemicellulose breakdown occurred between 210-320°C with minimal weight loss occurring beyond 320°C. Cellulose weight loss occurred predominantly between 310-390°C with almost no weight loss occurring outside that temperature range. Lignin showed the widest range of thermal degradation with weight loss occurring between 200-550°C. Related research done by Yang *et al.* [21] on the pyrolytic behavior of hemicellulose, cellulose, and lignin had similar results, with the exception of lignin continuing to breakdown up to 900°C. Since torrefaction occurs within the temperature range of 200-300°C, thermal degradation of hemicellulose, cellulose, and lignin will occur during torrefaction, as previously shown [16].

As previous literature has shown, torrefaction can greatly improve the energy content of a biomass when compared to raw biomass, making it a more suitable fuel for gasification or co-firing applications. Observations of combustion characteristics of torrefied rice husks and raw rice husks in a fluid bed combustor showed that the torrefied fuel ignited faster [22], this being attributed to the lower moisture content of the torrefied fuel. Bridgeman *et al.* [13] observed similar results when testing the effect of exposing torrefied willow to a methane-air flame. It was also noted that the combustion of char and volatiles was more exothermic, exothermic reactions being desirable for gasification to maintain constant reaction during the gasification process. Furthermore, char combustion of the torrefied fuel occurred more quickly but lasted longer than char combustion of raw fuel.

Most research on torrefaction of various biomass has resulted in the same conclusions. Mild torrefaction temperatures (240-250°C) produce biomass that is hydrophobic in nature [3] while the resulting heating value yield remains relatively high. Residence temperature has been shown to have a much greater effect upon the chemical changes than residence time. Previous work [3] has indicated that residence times beyond one hour have no significant impact upon the fuel

properties of biomass. The weight loss that occurs from mild torrefaction is highly dependent upon the hemicellulose fraction of the biomass being torrefied due to the thermal degradation of hemicellulose occurring below 280°C. It is apparent from literature that no research has investigated using CO₂. Furthermore, the three biomass used in this research have yet to be investigated as a torrefaction biomass. Therefore, the overall objective of this research was to investigate the effect of using CO₂ on torrefaction and pyrolysis of biomass as well as the effect of using CO₂ on the biomass fuel properties. TGA and DTG analysis is expected to provide a broad picture of the thermal break down of hemicellulose, cellulose, and lignin, and ultimate a proximate analysis provides insight into the effect of various carrier gasses upon the fuel properties of torrefied biomass. Careful analysis of the results obtained will explore the potential of CO₂ as a carrier gas for torrefaction. The following tasks were performed in order to achieve the objective of the research:

1. Obtain thermo-chemical characteristics of the raw biomass via:
 - a. Proximate Analysis
 - b. Ultimate Analysis
 - c. Heat Value Analysis
2. Determine the torrefaction characteristics of each biomass using a TGA by varying the residence temperature between 200-300°C in a Nitrogen environment.
3. Determine the effect of the purge gas upon the torrefaction of each biomass by:
 - a. Torrefying each biomass between 200-300°C in a Carbon-Dioxide and Argon environment.
 - b. Perform DTG analysis on the data obtained from the TGA for comparison.
4. Torrefy each biomass at a preferred torrefaction temperature in a laboratory oven in the following environments: Nitrogen, Carbon-Dioxide, and Argon.
5. Determine thermo-chemical characteristics of torrefied biomass as outlined in task 1.
6. Determine the effect of torrefaction upon the biomass via grinding and sieve analysis.
7. Investigate the effect of torrefaction upon the hydroscopic nature of the raw biomass.

3. EXPERIMENTAL TORREFACTION STUDY

In order to complete the outlined objectives several tests needed to be completed utilizing different pieces of equipment. The data used to create TGA thermograms and DTG curves were obtained from the TGA located in the Coal and Biomass Energy Lab (CABEL) at Texas A&M University (TAMU) in College Station, TX. The torrefaction of raw biomass samples for further testing was completed using a laboratory oven located in the CABEL at TAMU. Torrefied samples were sent to a commercial laboratory for further analysis.

3.1 Experimental Facility

3.1.1 ThermoGravimetric Analyzer

All TGA tests were performed utilizing a TA Instruments Q600 thermal analyzer located at the CABEL at Texas A&M University. The instrument is capable of highly reproducible measurements with $\pm 1\%$ accuracy. A schematic of the TGA setup used is shown in Fig. 3.1 below. The purge gasses were connected using one-eighth inch O.D. polyethylene tubing. The purge gas flow was regulated to below 20 psi using a pressure regulating valve attached to the purge gas tank.

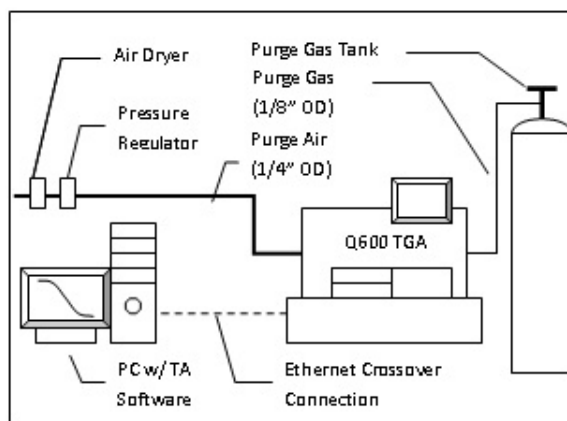


Fig. 3.1 - Schematic of the TGA setup used during experimentation (Adapted from [23])

During experiments the flow rate of the purge gas was controlled via the TA Instrument Explorer software installed on the connected PC and regulated via the internal mass flow controller in the Q600. Purge air was used after each test run to cool the furnace back to an ambient temperature. Detailed explanation of the operation principles of the TA Q600 can be found in Appendix A.

The TA Instrument Explorer software allows for direct control of several test parameters and can also be utilized to create a step by step test procedure. Two separate test procedures were used for the torrefaction and pyrolysis tests completed with the Q600. These procedures will be explained in further detail in subsequent sections.

3.1.2 *Laboratory Oven*

Due to the small sample size used in the TGA a Thermo Scientific Series 1284 laboratory oven (model F47925-80) was used to torrefy larger sample sizes of biomass that were used for thermo-chemical analysis. The laboratory oven allowed for a segmented test procedure to be programmed and run. The oven operates using open coil electric resistance heating elements controlled by a well insulated controller. The oven is insulated with ceramic fiber insulation. The F47900 series can operate from ambient temperatures up to 1093°C. A schematic of the laboratory oven setup can be seen below (Fig. 3.2).

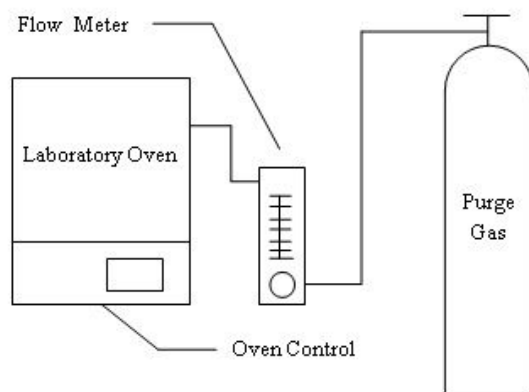


Fig. 3.2 – Schematic of the laboratory oven setup used to torrefy raw biomass.

The purge gas flow was regulated to just below 20 psi by a pressure regulating valve attached to the purge gas tank. The flow rate was controlled by a Dwyer series RMB flow meter. The regulator valves were connected to the flow meter using one-quarter inch O.D. polyethylene tubing. The outlet port of the flow meter was connected to the furnace via one-quarter inch O.D. stainless steel tubing due to the high temperatures inside the furnace. The specific test procedure used for analysis will be discussed in subsequent sections.

3.2 Experimental Procedure

3.2.1 Sample Preparation

The samples of Juniper and Mesquite were received in chip form with an initial size distribution between 2-4mm. The raw samples were utilized in the laboratory oven tests. However, further preparation was required for use in TGA experimentation. For this, the raw wood samples were further ground using a hand mill and sieved using a CE Tyler Roto-Tap model B. From the sieved samples it was determined that the largest particle size that would allow for an adequate sample amount during TGA experimentation were samples between 589-840 μ m samples. The 589-840 μ m fraction of the ground samples were removed and placed in airtight plastic bags and stored until needed.

The Sorghum received was of adequate size to be used for TGA experimentation. However, for consistency the raw Sorghum was sieved in the same manner as the Mesquite and Juniper samples. The 589-840 μ m fraction was removed and stored in an airtight plastic bag until needed.

3.2.2 Thermogravimetric Analysis

The TA Instruments software compatible with the Q600 was installed upon windows based system running Windows XP as its operating system. The software allows for the control of several test variables as well as the setup of a segmented program. For all TGA tests the setup procedure used was the following:

1. The furnace was opened and the reference cup (Fig. 3.3) was inspected to ensure it was clean and empty.
2. The test pan (Fig. 3.3) was removed and cleaned of any residual material if it had been used in a prior experiment. A new test cup was used for each different biomass tested and the same cup was used for the entirety of experimentation with one

biomass. Both the test and reference cup were 90 μl alumina pans obtained from TA Instruments.

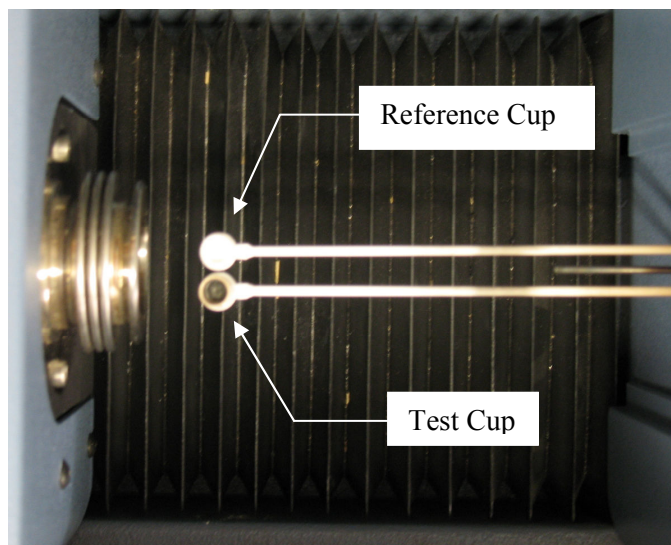


Fig. 3.3 – The TGA beams with empty reference and test pans.

3. The test cup was placed back on the empty test beam and the furnace was closed.
4. The instrument was tarred twice to ensure a proper zero reading.
5. Once tarred the furnace was again opened and 9-10 mg of sample was loaded into the test cup.
6. The TGA was purged for 5 minutes prior to any test run to ensure that the environment inside the furnace consisted of only the desired gas (Nitrogen, Carbon-dioxide, Argon). The purge flow rate was the same as the flow rate used for experimentation, 200ml/min.
7. The mass flow control within the TGA is calibrated for use with Nitrogen. In order to determine the correct flow rate value required for use with Argon and Carbon-dioxide a k-factor method was used as recommended by TA instruments:

$$\text{Flow Rate Set Point} = \frac{\text{Flow Rate}_{\text{Nitrogen}}}{K \text{ factor new gas}} \quad (2)$$

The flow rate was 200ml/min for all experiments done using the TGA. The k-factors of the gasses used for experimentation are as follows:

Ar – 1.42

CO₂ - 0.74

8. Once the flow rate had been set and the furnace had been purged the proper segmented program was run using the TA Instruments software.

Each experiment was repeated at least once to test repeatability and accuracy of the results obtained.

3.2.2.1 TGA Segmented Program

For the pyrolysis experiments the segmented program consisted of a single step:

1. A constant heating process at a constant heat rate of 20°C/min to 1000°C

For the torrefaction experiments a program consisting three steps was used. The process first torrefied the biomass and then pyrolyzed the remaining biomass. The segmented program involved the following steps:

1. An initial heating ramp at a constant heating rate (20°C/min.) to a desired temperature (torrefaction temperature.)
2. An isothermal process in which the biomass was kept at a steady temperature for one hour. This process resulted in the fuel being torrefied.
3. The biomass then underwent another heating ramp at a rate of 20°C/min until the furnace temperature reached 1000°C. This final step pyrolyzed the torrefied biomass.

The residence temperatures tested were in the range of 200-300°C with a 20°C increment. For each biomass three different purge gasses were tested at each residence temperature. Straight pyrolysis experiments were also completed (constant heating rate, no isothermal torrefaction process) using each biomass with three different purge gasses. A total of forty-two tests were completed using the Q600. During each experiment the measurements were recorded every 20 seconds for the entirety of the experiment. The data was stored in a text file that was imported into Excel for data analysis.

3.2.2.2 *Laboratory Oven*

The Thermo Scientific Series 1284 laboratory oven allowed for the programming of up to eight different procedure segments. On the basis of reviewed literature and the initial TGA tests it was determined that 240°C was the optimal temperature for the torrefaction process. This was the only residence temperature used for the laboratory oven tests. The following procedure was used for carrying out the torrefaction of raw biomass in the laboratory oven:

1. The ceramic test crucibles used in the laboratory oven were cleaned of all residues from previous tests.
2. The crucibles were filled with 5-6 grams of sample and placed inside the laboratory oven at room temperature.
3. Once the samples were in the oven the purge gas flow was set. The nominal flow rate used was 12.5 SCFH. This flow rate was found, from previous experiments, to be an adequate flow to maintain a purge within the oven. Since the flow meter was designed for use with air the flow rate for each carrier gas was determined using the following:

$$\frac{\dot{m}_{new\ gas}}{\dot{m}_{air}} = \sqrt{\frac{\rho_{new\ gas}}{\rho_{air}}} \quad (3)$$

4. Once the flow rate was set the oven was allowed to purge for 5 minutes prior to beginning any tests.
5. Once the oven was sufficiently purged a predefined segmented program was run. The program consisted of the following steps:
 - a. A constant heating ramp at a rate of 20°C/min to 240°C
 - b. An isothermal torrefaction process held at 240°C for 60 minutes
 - c. Heating was stopped and power to the heat coils was shut off
6. In order to ensure that each of the samples were torrefied for 60 minutes, the tests were timed and the samples were removed from the oven immediately after the completion of torrefaction. The torrefied samples removed from the oven were placed in a desiccator and allowed to cool.
7. After the samples were cooled, they were placed inside airtight plastic bags.

Each biomass was torrefied at 240°C using all three purge gases, resulting in nine total samples torrefied. Roughly 40 grams of each biomass was torrefied and sent for fuel property analysis.

3.2.3 *Torrefied Fuel Properties*

Both raw and torrefied samples were shipped to a third party commercial evaluation laboratory for fuel property analysis. The following tests were carried out on the raw and torrefied biomass samples:

1. Proximate Analysis
2. Ultimate (Elemental) Analysis
3. Heat Value Analysis

Results of the analysis were reported on an as received and dry basis.

3.2.4 *Grindability Analysis*

After large scale torrefaction using the laboratory oven, torrefied and raw biomass samples were tested for grindability. The grindability tests consisted of sieve analysis (size distribution analysis) and sample grinding using a Sweco model DM1 grinding mill. All samples were ground for 20 minutes so that the amount of energy used in grinding the samples was held constant. The procedure for grindability testing is as follows:

1. Samples underwent sieve analysis in accordance with ASTM standard D4749-87. The following sieves were used:

Seive #	Mesh Size (μm)
8	2360
10	2000
20	850
30	600
100	150
200	75
270	53

Prior to sieving the total mass of sample undergoing analysis was weighed and recorded. A CE Tyler Roto-Tap model B shaker was used to sieve the fuel and from preliminary measurements it was determined that 30 minutes was an adequate sieve time.

2. After shaking the mass of sample retained in each sieve was weighed and recorded to obtain an initial size distribution.
3. Once an initial size distribution had been found the samples were ground for 20 minutes.
4. The total mass of the ground sample was then weighed and recorded. The ground sample was then sieved and weighed in the manner outlined in steps 1 and 2.

Based upon previous TGA/DTG and laboratory oven results it was determined that torrefaction using Nitrogen and Argon produced the very similar results. Therefore, grindability tests were conducted using raw biomass and biomass torrefied in a Nitrogen and Carbon-dioxide environment.

3.2.5 Hydrophobicity Test

Biomass samples torrefied in the laboratory oven also underwent hydrophobicity testing to see how torrefaction affected the amount of moisture the biomass would absorb. Previous research has stated that torrefaction results in a biomass that is hydrophobic in nature. The following procedure was used to test moisture the hydrophobicity of both raw and torrefied biomass:

1. The initial weight of the biomass sample being tested was measured and recorded.
2. The sample was then submerged in water for 15 hours
3. After soaking for 15 hours the sample was removed from the water by straining it through a 45 μ m mesh and then weighed.
4. Next, a portion of the soaked sample underwent moisture testing by heating the sample for a minimum of 12 hours in the laboratory oven (ASTM standard D3173) to determine the moisture content of the soaked biomass.

3.3 Data Analysis

3.3.1 TGA Thermograms

The data collected by the TGA can be analyzed in a many ways. The most basic analysis of TGA data is in the creation of thermograms which plot the weight loss of the substance being tested versus temperature (time can also be used as the x-axis). A sample TGA thermogram can be seen in Fig. 3.4. Thermograms give a basic picture of the thermal breakdown of a substance over a given temperature range.

In general a thermogram shows the temperature range over which drying and pyrolysis occurs. The mass loss in the drying zone can be attributed to moisture present in the sample lost during drying. Point A in Fig. 3.4 shows the end of the drying zone for the sample thermogram. The start of pyrolysis is indicated by point B, this is the point when the volatiles within the substance begin to breakdown and are released in gaseous form.

The pyrolysis zone of lignocellulosic biomass can be divided into two zones as done by Mensaray and Ghaly[18]. The first zone being termed the “active pyrolysis zone” with research attributing this zone to the liberation of low weight volatiles and evolution of more complex volatiles. The end of the active pyrolysis zone is indicated by point C and coincides with the start of the “passive pyrolysis zone”. The mass loss in the passive pyrolysis zone can be attributed to further evolution of volatiles and the conversion of lignin, ending around 500°C indicated by point D. The mass remaining after pyrolysis is mainly ash and char. The shift from active to passive pyrolysis is indicated by a significant change in the slope of the weight trace.

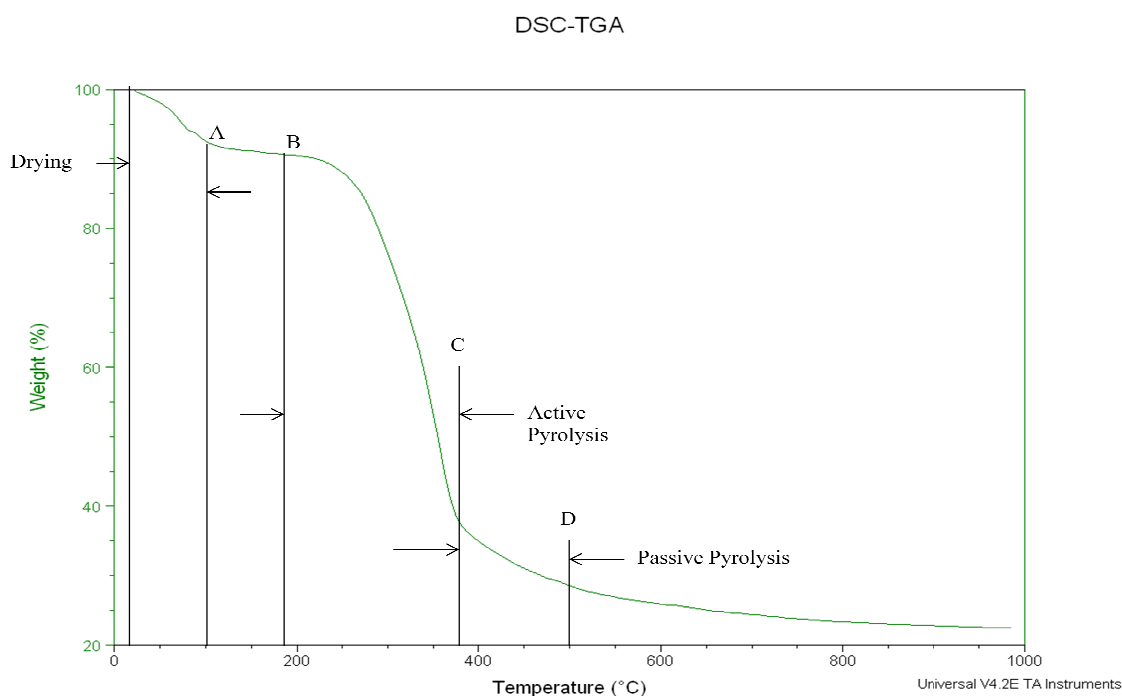


Fig. 3.4 – Sample thermogram from the pyrolysis of lignocellulosic biomass.

3.3.2 DTG Analysis

Another type of analysis that can be done from TGA data is DTG (Derivative Thermogravimetric) analysis. DTG analysis provides a method in which the thermochemical degradation of the different constituents of a material can be quantified. A sample DTG graph can be seen in the figure below (Fig. 3.5).

Based upon the DTG distribution one can clearly observe three different peaks which corresponds to the temperature ranges over which hemicellulose, cellulose, and lignin breakdown occurs during the pyrolysis process. The initial peak on the far left of the DTG chart in Fig. 3.5 is due to drying and exhibits the moisture lost from the biomass during this process. The first major peak corresponds to the peak breakdown of hemicellulose during pyrolysis. Hemicellulose has been found to breakdown over the temperature range of 210-350°C [18]. The second peak corresponds to the peak breakdown of cellulose within the biomass, cellulose breaking down over the temperature range of 310-390°C. Finally the last peak corresponds to the breakdown of lignin, which degrades over the temperature range of 200-550°C. Lignin is a more complex chemical compound and therefore has a wider temperature range over which it breaks down.

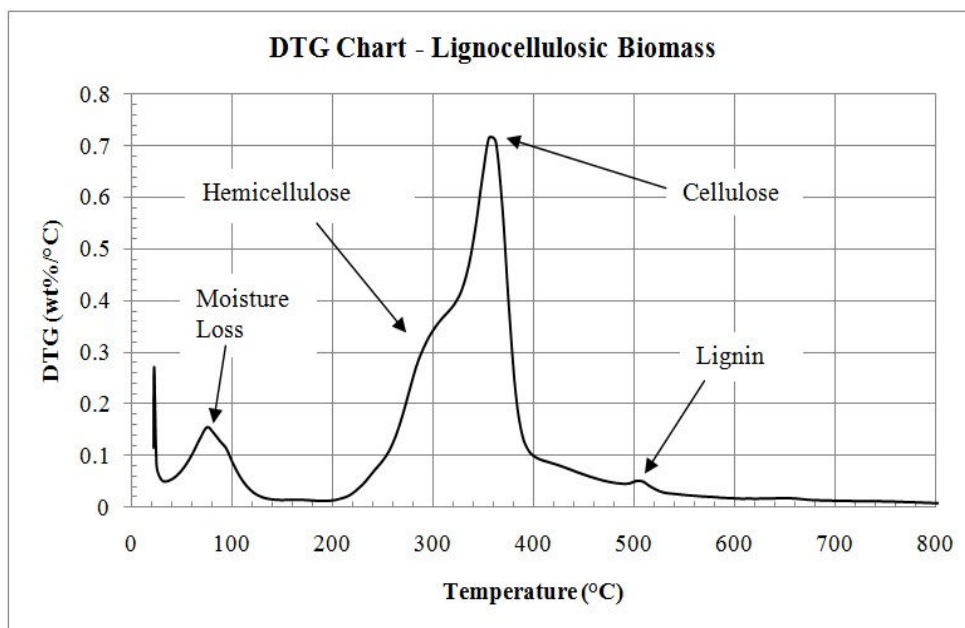


Fig. 3.5 – Sample DTG chart of lignocellulosic biomass.

DTG charts can be used in conjunction with TGA thermograms to extract a great deal of information about the thermal degradation of a biomass on one chart. A sample TGA/DTG chart can be seen in Fig. 3.6 below. From a TGA/DTG chart it is one can readily relate the weight loss at a given temperature to the thermal breakdown of a certain constituent or multiple constituents within a biomass. For example, in the sample TGA/DTG chart shown below it can be seen how the initial weight loss can be attributed to drying of the biomass. It is also important to note that after the initial mass loss due to drying, any further mass loss from pyrolysis is entirely from the thermal degradation of hemicellulose, cellulose, and lignin.

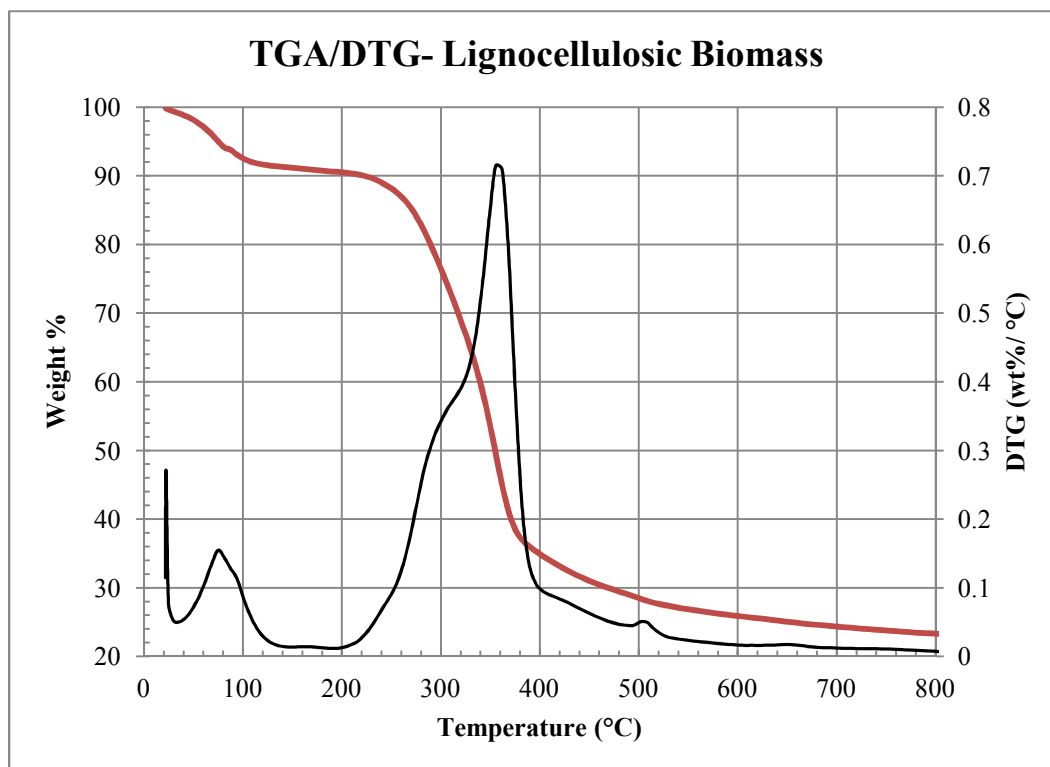


Fig. 3.6 – Sample TGA/DTG chart for lignocellulosic biomass.

4. RESULTS AND DISCUSSION

4.1 Introduction

Initial TGA/DTG analysis was conducted to determine the effect of torrefaction temperature and purge gas had upon the biomass. A wide range of torrefaction temperatures (200-300°C) was investigated in order to provide a complete representation of the effect of varying torrefaction temperatures on the thermal breakdown of the biomass tested. The optimal torrefaction temperature was obtained by observing the weight loss characteristics of the biomass from thermograms and observing the thermal breakdown of hemicellulose, cellulose, and lignin from DTG distributions.

Both TGA thermograms and DTG distributions were created and analyzed to determine the effect of each purge gas upon the torrefaction of each biomass. Nitrogen was used as the base case for this analysis as nearly all previous research reviewed in literature utilized Nitrogen as the purge gas. Comparisons were made between each purge gas for each biomass by observing the changes in peak breakdown of hemicellulose, cellulose, and lignin on DTG distributions as well as weight loss trends on thermograms.

After primary TGA/DTG analysis, the optimal torrefaction temperature was determined and used as the torrefaction temperature for laboratory oven tests. Torrefied samples from the laboratory oven underwent fuel property analysis and the results of fuel property analysis were compared to determine the effect, if any, altering the purge gas had upon the fuel properties. Further research was done to determine the effect torrefaction had upon the grindability of the biomass as well as the hydrophobic properties of the torrefied biomass.

4.2 Raw Biomass Fuel Properties

Prior to doing any experimentation the raw biomass samples were sent to a third party lab for fuel property analysis. The results of proximate, ultimate, and heat value analysis are presented in Table 4.1. Upon initial inspection there are slight differences in the three biomasses being used. The Mesquite wood has a high moisture content (15.53%) compared to the other two biomasses. The Juniper wood has a higher VM content (77.99%) and lower moisture content

(5.85%) then both Sorghum (VM: 65.34%, MC: 8.23%) and Mesquite (VM: 66.09%, MC: 15.53%). The Sorghum has a high amount of ash (9.62%) which will cause it to have a slightly different thermal degradation profile as shown in subsequent sections. All three biomass have relatively the same FC content with Juniper having only a slight lower FC content than Mesquite and Sorghum.

Table 4.1 – Proximate, ultimate, and heat value analysis of the raw biomass used for experimentation (reported on an as received basis unless otherwise noted.)

	Raw Biomass		
	Mesquite	Juniper	Sorghum
Moisture	15.53	5.85	8.23
Volatile Matter	66.09	77.99	65.34
Fixed Carbon	16.71	14.25	16.81
Ash	1.67	1.91	9.62
Carbon	43.60	49.27	45.78
Oxygen	33.57	37.00	30.17
Hydrogen	4.98	5.68	5.01
Nitrogen	0.62	0.28	1.08
Sulfur	0.03	0.01	0.11
HHV (kJ/kg)	16666	18987	15928
HHV _{DAF} (kJ/kg)	20128	20584	19389
Empirical Formula *	CO _{0.58} H _{1.37} N _{0.012} S _{0.0003}	CO _{0.56} H _{1.38} N _{0.005} S _{0.0001}	CO _{0.49} H _{1.31} N _{0.02} S _{0.0009}
Note: Results on an AR basis unless otherwise noted			
* - Formula Carbon normalized			

The ultimate analysis further demonstrates the variations between the three biomass samples. The Carbon and Hydrogen content of Juniper is the highest amongst the three biomass; as a result its HHV is the largest. The results of heat value analysis illustrate how the varying ash and moisture content of the three biomass effect their energy contents. The high ash content of Sorghum is the main cause of its HHV being the lowest (on an as received basis) of the three

biomass samples. Similarly, the high moisture content of Mesquite causes its HHV to be lower. Although the Oxygen content of Juniper is the highest, its ash and moisture content are low ultimately resulting in Juniper having the largest HHV. For further reference the raw biomass properties are presented on a dry and dry ash free basis in Appendix B.

Comparing the raw biomass to two coal samples that have been used previously in the CABEL (Table 4.2), one can clearly see why coal is a better fuel for combustion. Although the moisture content of both Texas Lignite (TXL) and Powder River Basin (PRB) coal is much higher than the raw biomass samples, the oxygen content of the coal much lower than the raw biomass. This as well as a higher FC content is what cause both coals to have a larger HHV compared to the three raw biomass samples.

Table 4.2 – Proximate, ultimate, and heat value analysis of Texas Lignite (TXL) and Powder River Basin (PRB) coal (reported on an as received basis unless otherwise noted). [13]

	Coal	
	TXL	PRB
Moisture	38.34	32.88
Volatile Matter	24.79	28.49
Fixed Carbon	25.41	32.99
Ash	11.46	5.64
Carbon	37.18	46.52
Oxygen	9.61	11.29
Hydrogen	2.12	2.73
Nitrogen	0.68	0.66
Sulfur	0.61	0.27
HHV (kJ/kg)	14287	18193
HHV _{DAF} (kJ/kg)	28460	29597
Empirical Formula	$C_{2.07}O_{0.6}H_{2.12}N_{0.049}S_{0.019}$	$C_{2.37}O_{0.71}H_{2.73}N_{0.047}S_{0.008}$

4.3 TGA

TGA Thermograms for each biomass and each carrier gas will be presented in this section. General trends observed from analysis of thermograms will be discussed. In depth discussion and formal conclusions will be presented after both the TGA and DTG results have been discussed in detail.

4.3.1 *Mesquite*

TGA analysis was carried out using the TA Q600 instrument. Analysis was carried out using the procedure detailed in section 3.2.2 of this thesis. All of the biomasses were tested on an as received basis. For simplicity the thermograms for each torrefaction temperature were overlaid on the same plot. The thermograms for pyrolysis and torrefaction of mesquite using N₂, Ar, and CO₂ as the purge gas can be seen in Fig. 4.1, Fig. 4.2, and Fig. 4.3 respectively.

The TGA thermograms for each purge gas have the same relative shape and can be broken down into different zones as described earlier. For torrefaction, each thermogram follows the weight loss curve for pyrolysis until reaching the torrefaction temperature. At this point the thermogram follows a vertical line resulting from weight loss due to the sample being held at a constant temperature for the duration of torrefaction. Due to the nature of operation of the TGA the torrefaction thermograms show a slight oscillation at the beginning of torrefaction before reaching a true isothermal state of operation.

After torrefaction has been completed the thermograms follow a horizontal line that begins to curve before again following the weight loss curve from straight pyrolysis (no isothermal torrefaction process). This portion of the torrefaction thermograms coincides with what Chen and Kuo [7] called a “chemically frozen” zone, in which nearly no reactions occur. In this chemically frozen zone the weight of the sample remains the same as the temperature increases. This is due mostly to volatiles of low bond strength being liberated during the torrefaction process, therefore a further increase in temperature is required to breakdown the more complex volatiles remaining after torrefaction.

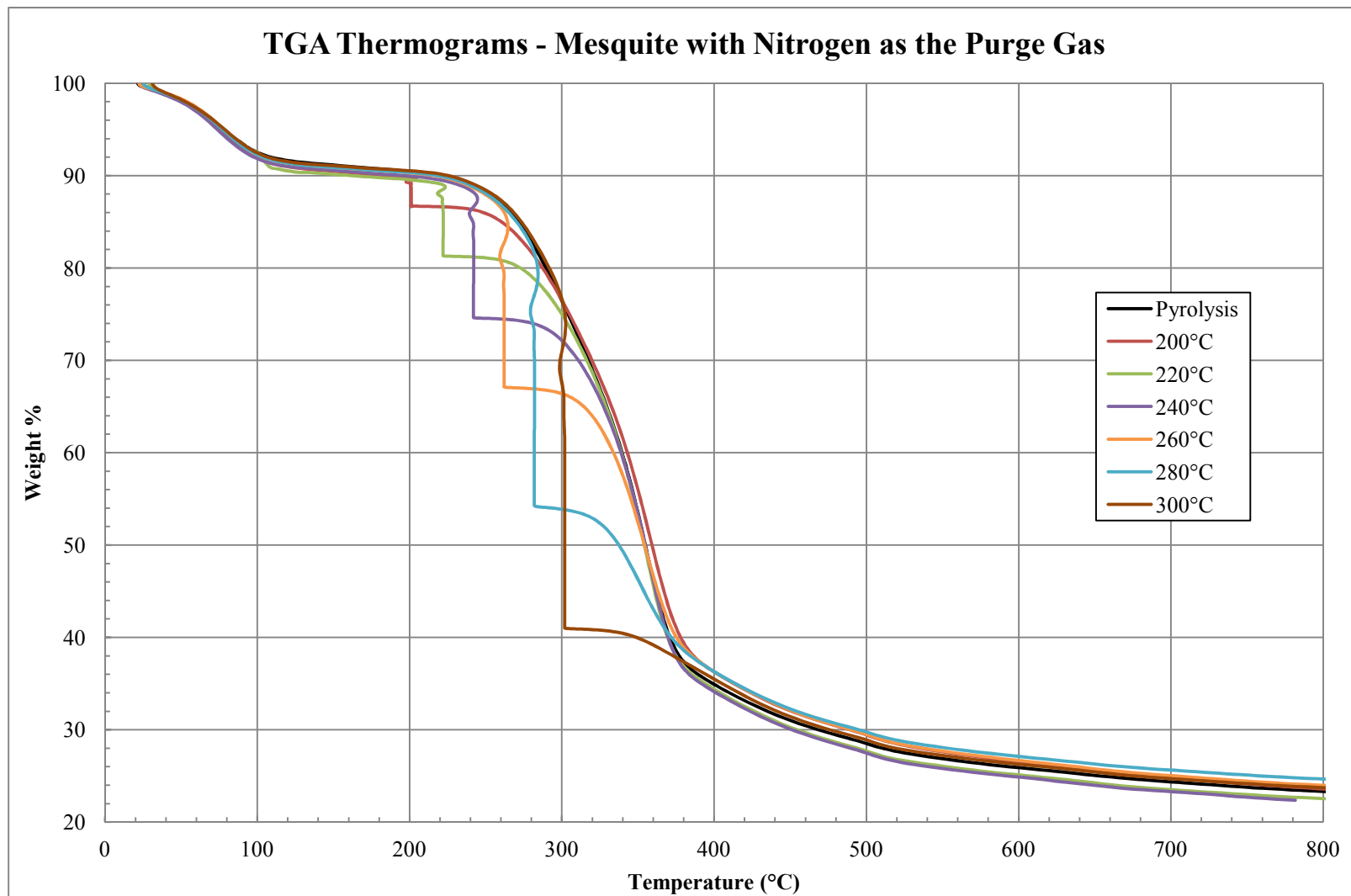


Fig. 4.1 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using N₂ as the purge gas.

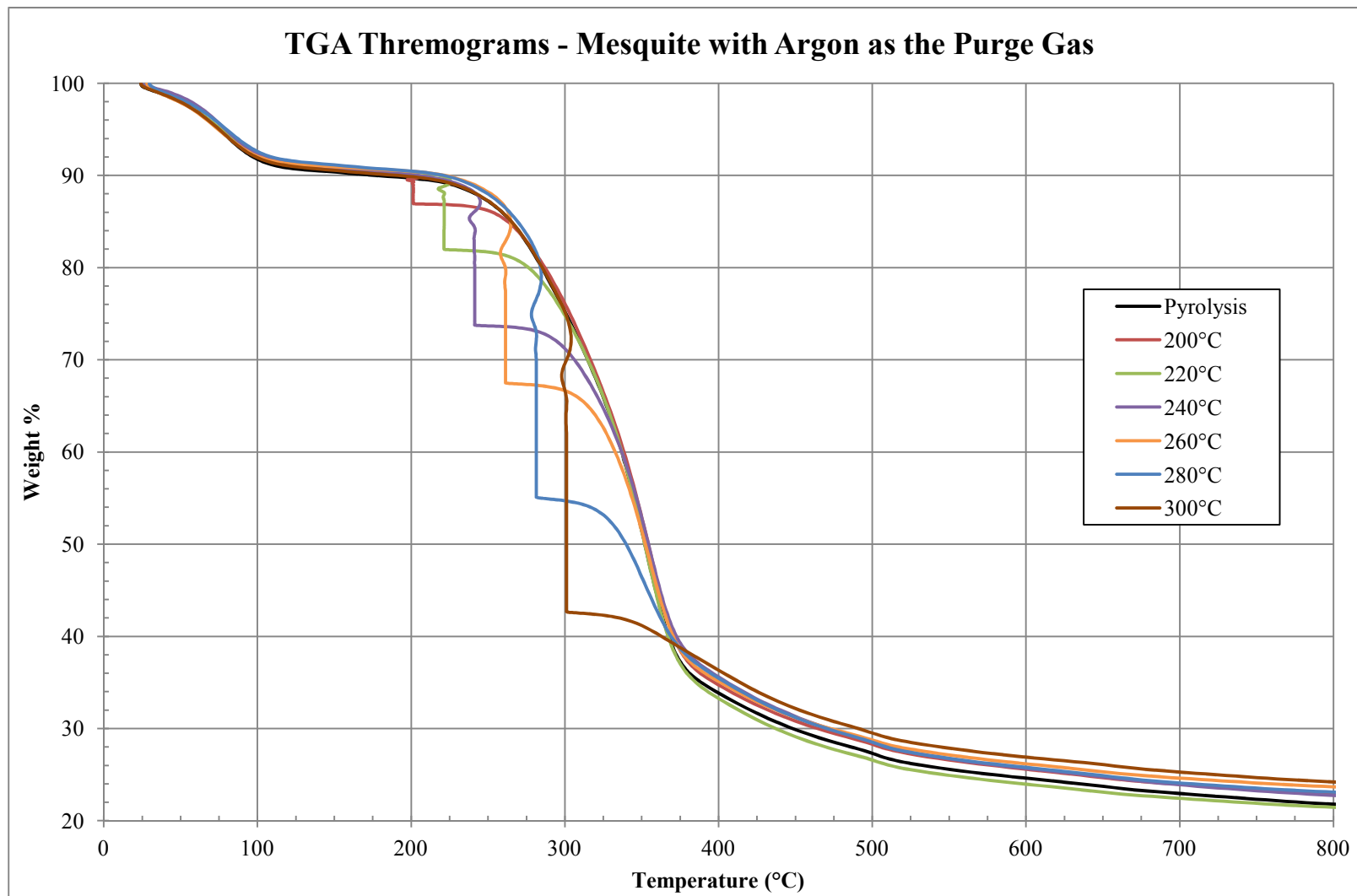


Fig. 4.2 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using Ar as the purge gas.

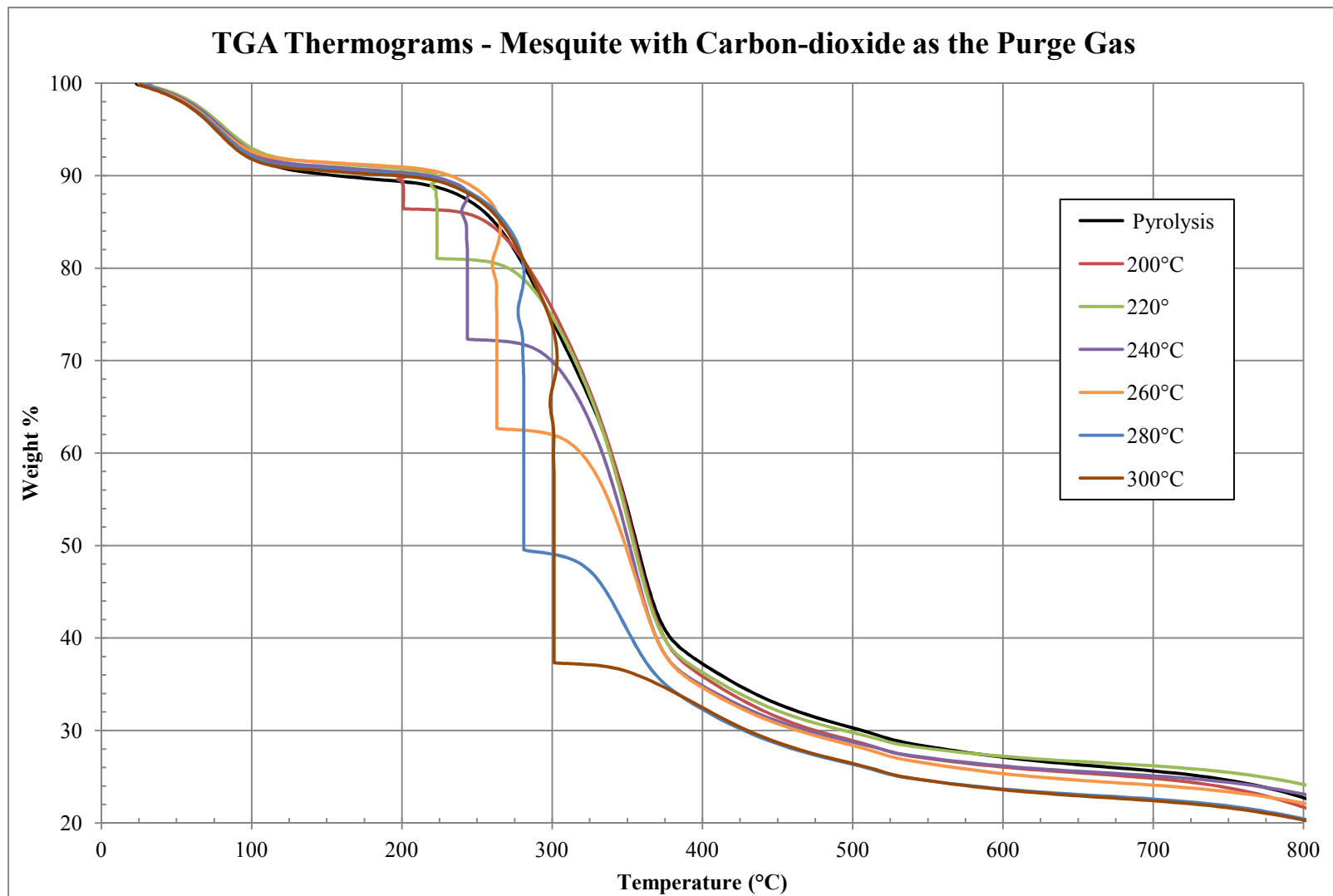


Fig. 4.3 - TGA thermograms of Mesquite wood pyrolysis and torrefaction using CO₂ as the purge gas.

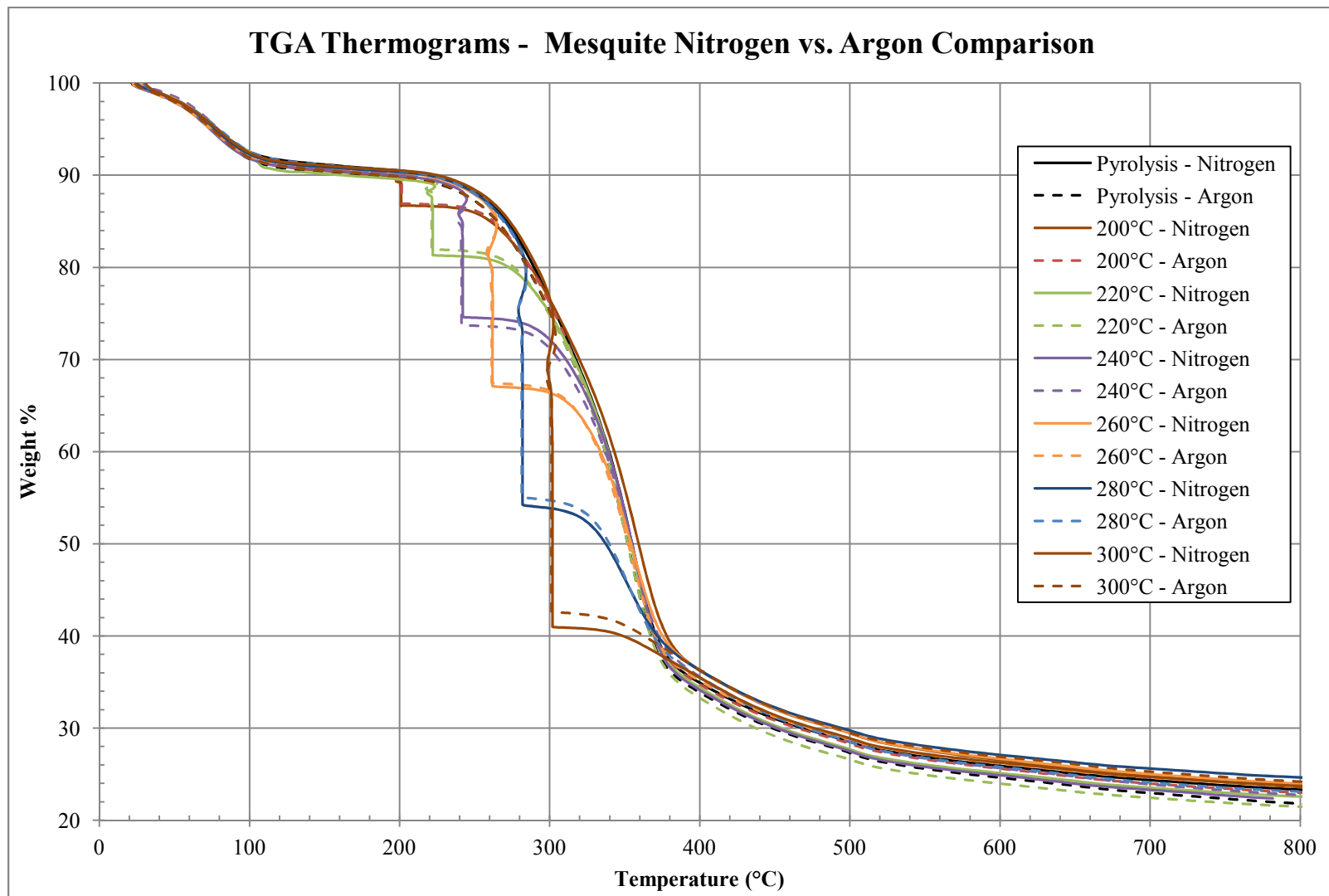


Fig. 4.4 - Comparison of thermograms from pyrolysis and torrefaction of Mesquite wood using N₂ and Ar as the purge gases.

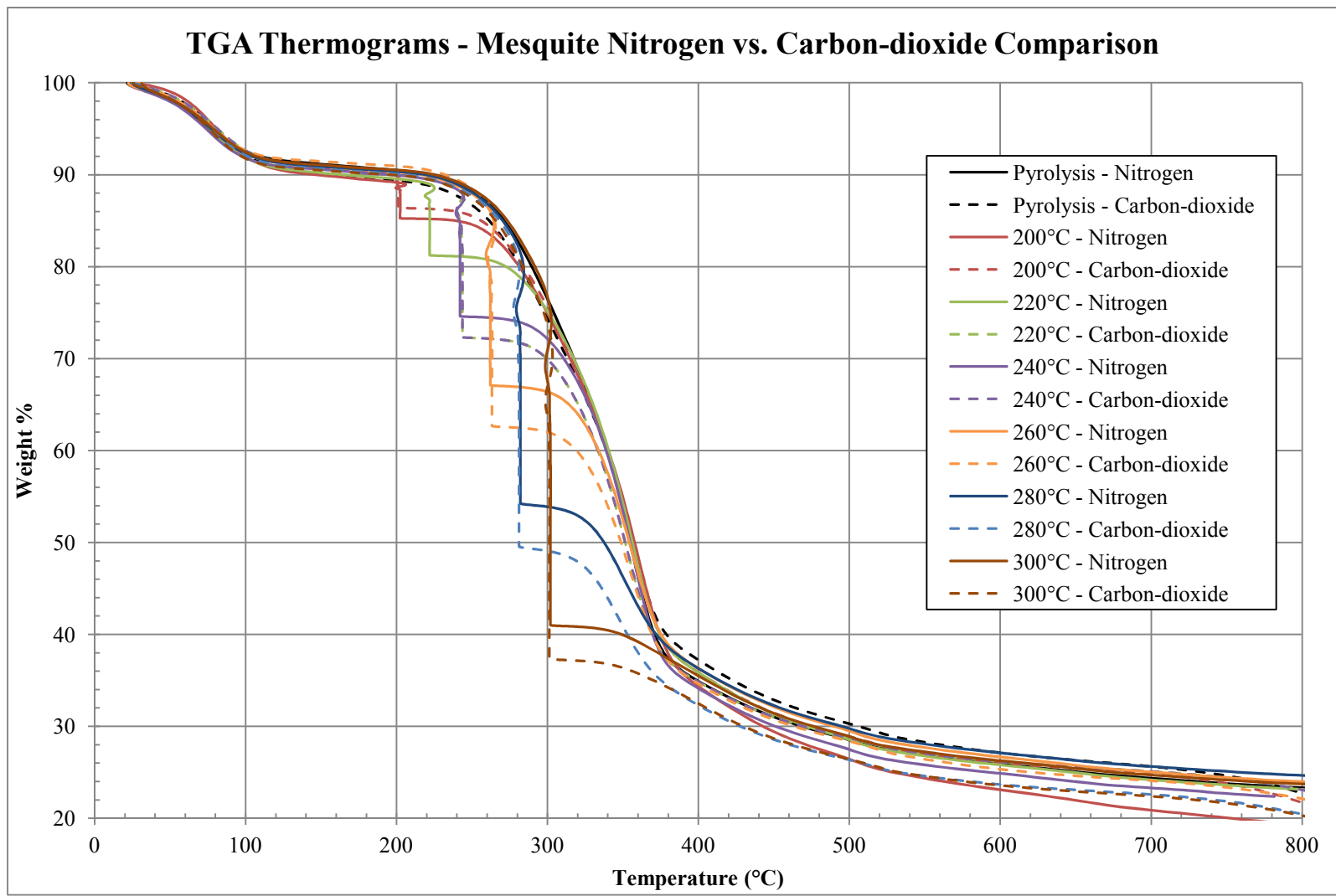


Fig. 4.5- Comparison of thermograms from pyrolysis and torrefaction of Mesquite wood using N₂ and CO₂ as the purge gases.

Overlaying the thermograms of samples that were pyrolyzed and torrefied using different purge gasses gives more insight as to the effect of the purge gas upon the breakdown of the biomass. Overlays of both Argon and Carbon-dioxide versus Nitrogen (the reference gas) can be seen in Fig. 4.4 and Fig. 4.5 respectively.

From initial inspection it is clear that there is very little difference in the thermograms from the pyrolysis and torrefaction in Nitrogen and Argon. Both Nitrogen and Argon exhibit roughly the same amount of weight loss at a given torrefaction temperature. Slight differences in weight loss between these two purge gases can be attributed to differences in the biomass samples being tested.

The shape of the biomass particles inherently has some variation due to sample preparation. The manner in which samples were loaded into the alumina TGA cups would also have caused some variations in sample, with tightly packed samples breaking down differently than loose packed samples.

Comparison of the thermograms using Nitrogen and Carbon-dioxide as the purge gas shows a noticeable difference between the two gases. For torrefaction temperatures above 240°C, samples torrefied using CO₂ as the purge gas have a higher amount of weight loss than samples torrefied using Nitrogen. This is due mainly to chemical reactions occurring between CO₂ and the Carbon within the fuel which will be discussed in further detail in a subsequent section.

4.3.2 *Juniper*

Data obtained from torrefaction and pyrolysis of Juniper wood chips was analyzed in the same manner as the data from Mesquite wood pyrolysis and torrefaction. TGA thermograms of torrefaction and pyrolysis using Nitrogen, Argon, and Carbon-dioxide as the purge gas can be seen in Fig. 4.6, Fig. 4.7, and Fig. 4.8 respectively.

The shape of the thermograms from Juniper wood follows the same trends as the thermograms from Mesquite wood. The only noticeable difference between the pyrolysis curves of Mesquite and Juniper being the weight percent remaining after the active pyrolysis zone. Juniper wood loses more weight during the initial active pyrolysis zone when compared to Mesquite due to differences in the chemical composition of the two biomasses.

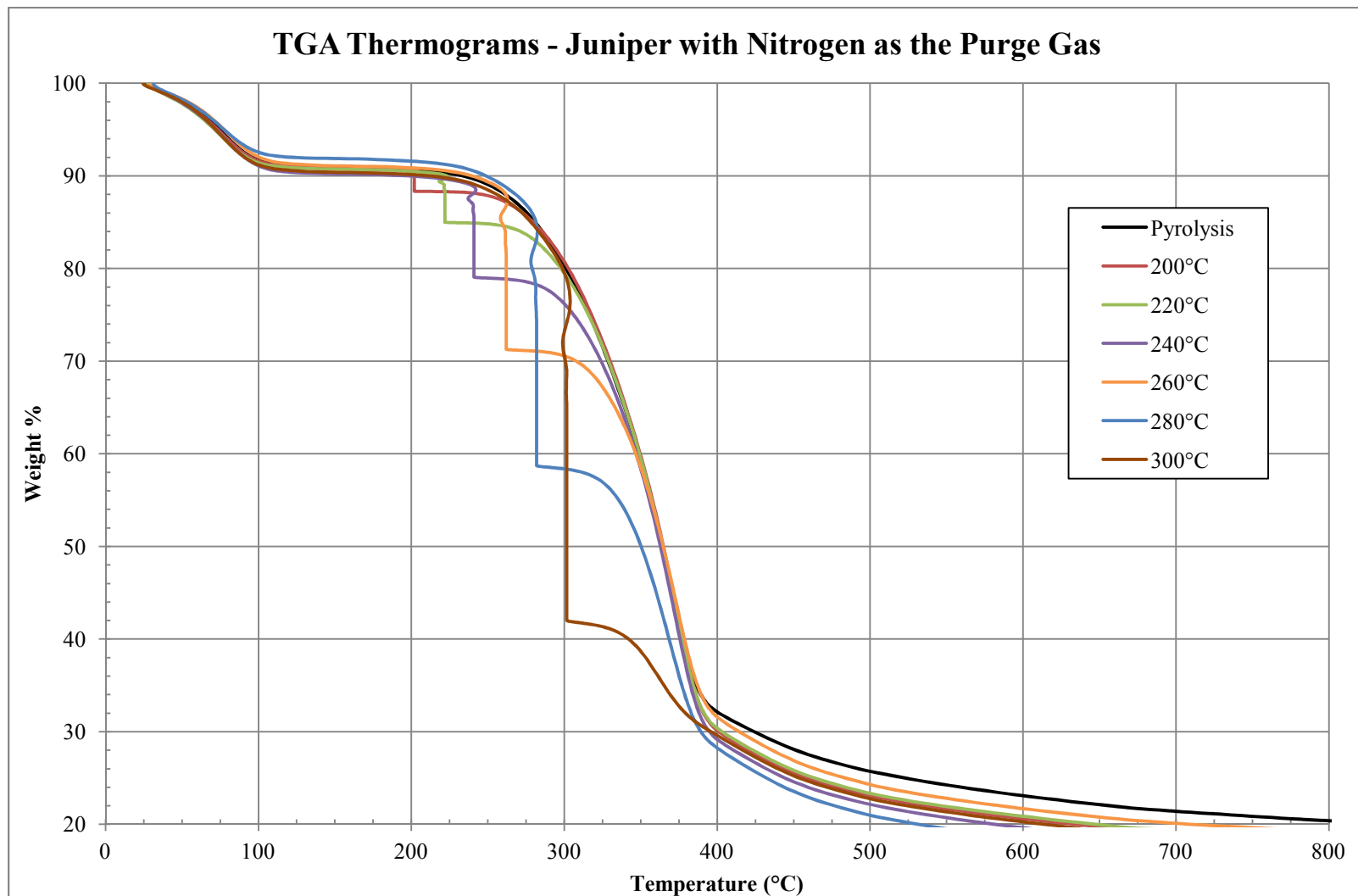


Fig. 4.6 - TGA thermograms of Juniper wood pyrolysis and torrefaction using N_2 as the purge gas.

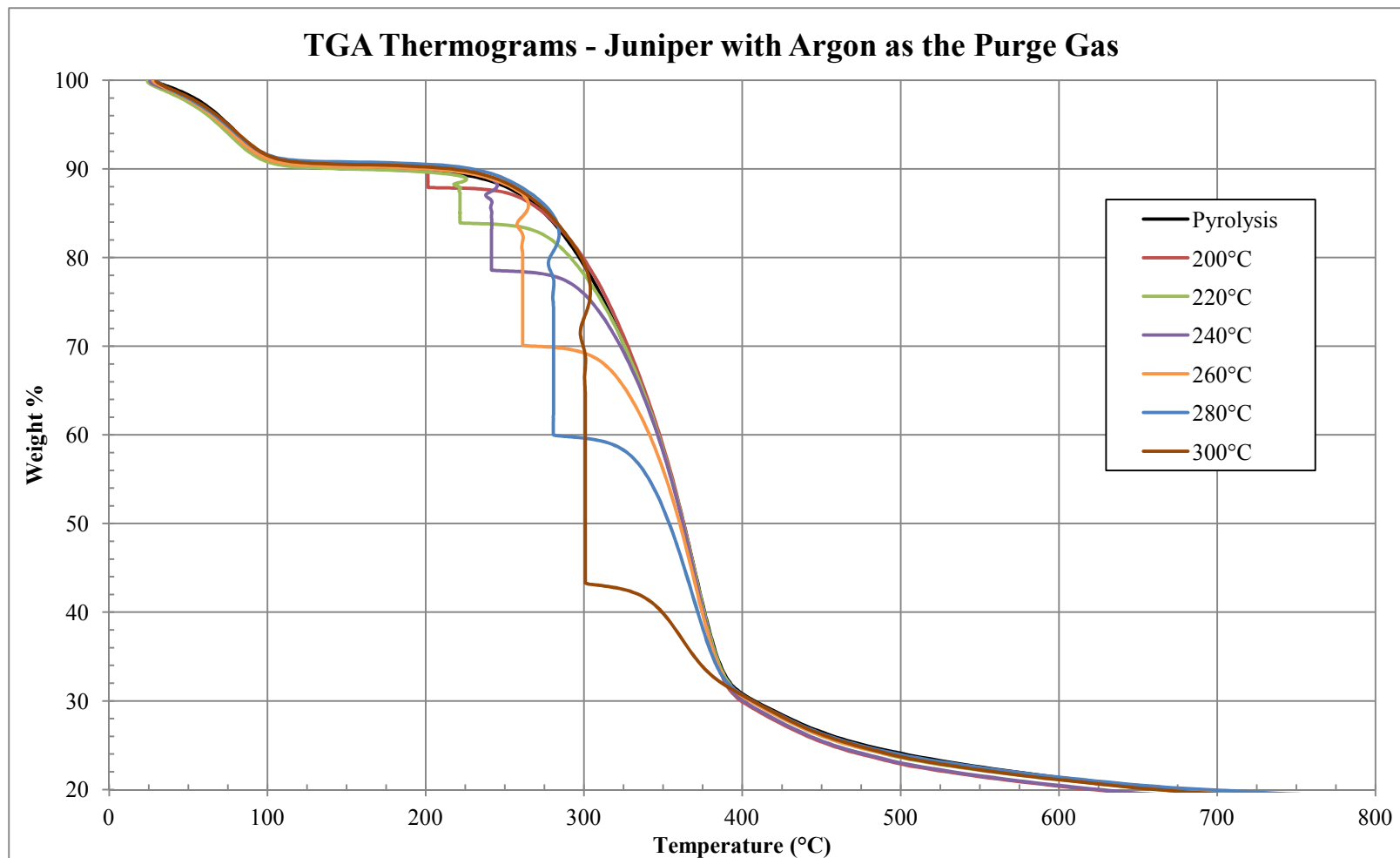


Fig. 4.7 - TGA thermograms of Juniper wood pyrolysis and torrefaction using Ar as the purge gas.

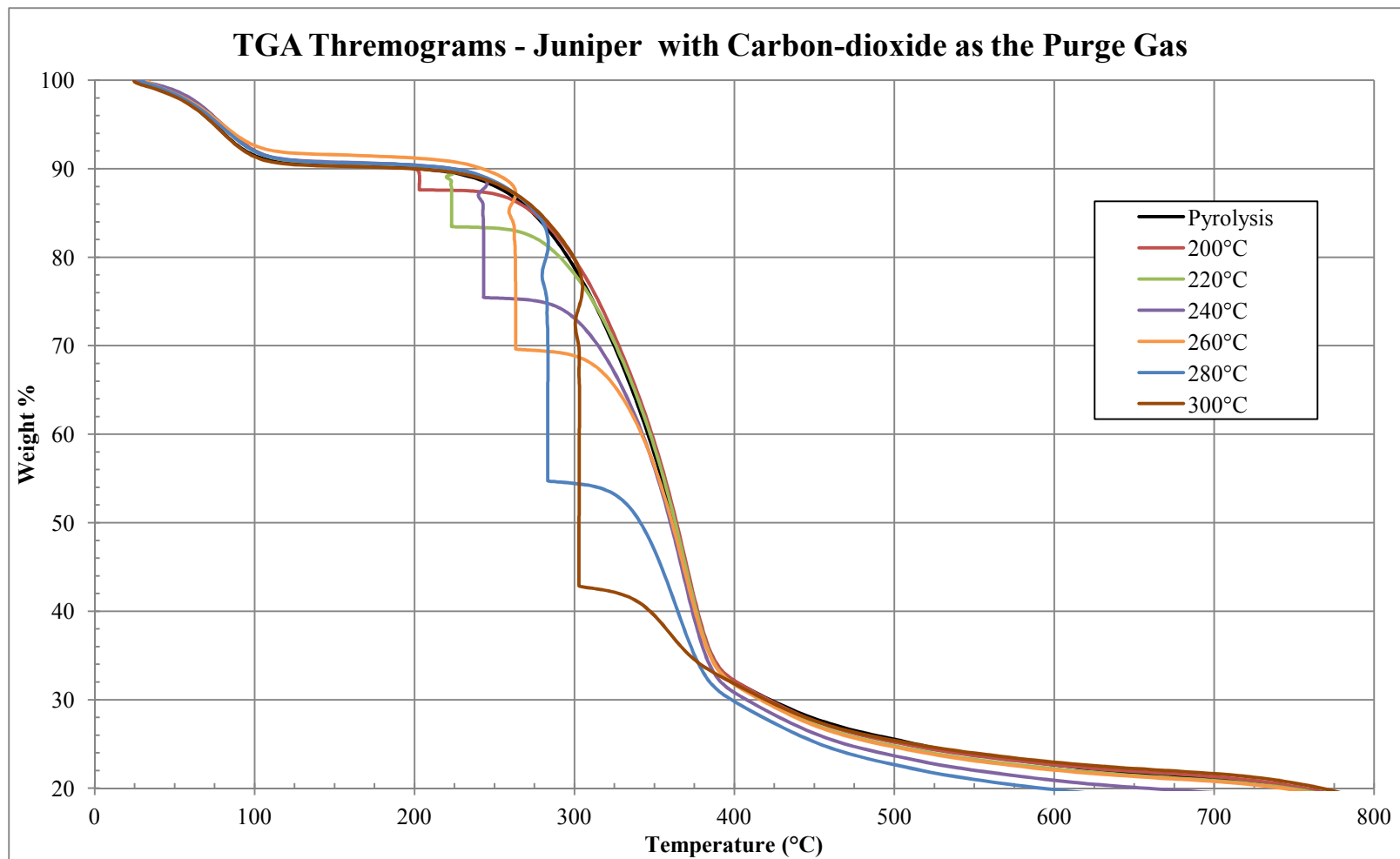


Fig. 4.8 - TGA thermograms of Juniper wood pyrolysis and torrefaction using CO₂ as the purge gas.

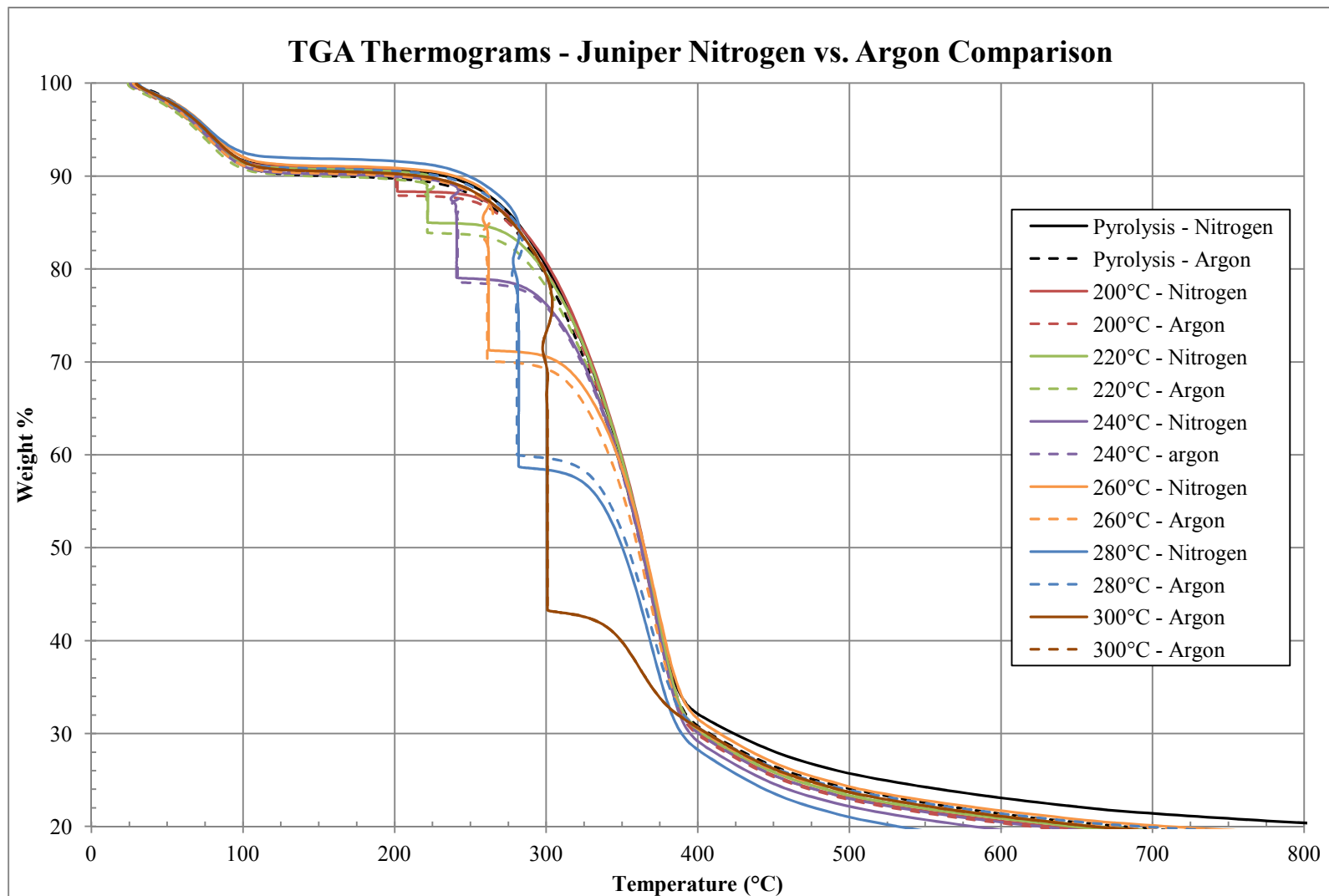


Fig. 4.9 - Comparison of thermograms from pyrolysis and torrefaction of Juniper wood using N₂ and Ar as the purge gasses.

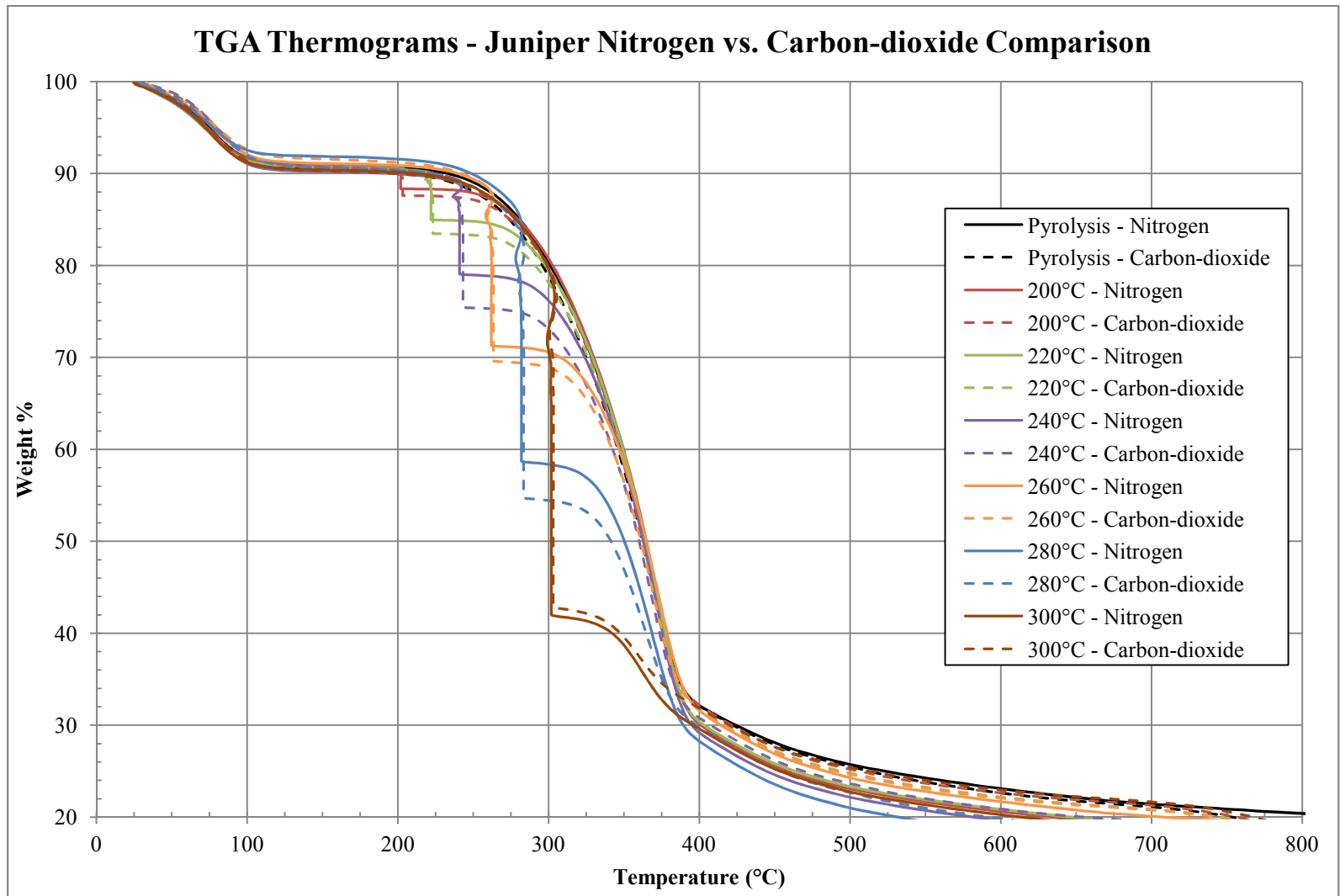


Fig. 4.10 - Comparison of thermograms from pyrolysis and torrefaction of Juniper wood using N₂ and CO₂ as the purge gases.

Comparing the weight loss from the torrefaction of Mesquite and Juniper wood it can be seen that Mesquite wood has a higher amount of weight loss at a given torrefaction temperature. This is due mainly to differences in the chemical composition of both biomasses. Prins *et al.* [8] has stated that deciduous woods, such as Mesquite, have a hemicellulose fraction comprised of mostly Xylan. Xylan being more reactive than Mannan, the main constituent of the hemicellulose fraction found in coniferous woods (such as Juniper). As discussed in section 2 of this thesis, due to the temperature range over which hemicellulose breaks down, a significant portion of the weight lost during torrefaction occurs from the decomposition of hemicellulose. Therefore, the hemicellulose fraction of Mesquite being more reactive than that of Juniper is the main cause for a higher weight loss during the torrefaction of Mesquite.

For further analysis of the effect of the purge gas upon the torrefaction of Juniper thermograms from the torrefaction and pyrolysis using Argon and Carbon-dioxide were overlaid with the thermograms using Nitrogen as the purge gas. These overlays can be seen in Fig. 4.9 and Fig. 4.10 respectively.

The trends observed from the comparison of Argon and Carbon-dioxide to Nitrogen appears similar to the ones observed from previous experiments with Mesquite. However there are some slight difference in the weight loss between Nitrogen and Argon. These differences are attributed slight variations in the samples tested. Comparison of the thermograms using Nitrogen and Carbon-dioxide as the purge gas shows that using Carbon-Dioxide results in a higher amount of weight loss. This holds true except for torrefaction carried out at 300°C, where tests using N₂ and CO₂ resulted in the same amount of weight loss.

4.3.3 Sorghum

Data obtained from torrefaction and pyrolysis of Sorghum was analyzed in the same manner as previous experiments. TGA thermograms of torrefaction and pyrolysis using Nitrogen, Argon, and Carbon-dioxide as the purge gas can be seen in Fig. 4.11, Fig. 4.12, and Fig. 4.13 respectively. The general trends observed for Mesquite and Juniper woods are also observed here.

Comparing the weight loss during torrefaction of all three biomasses shows that in general torrefaction of sorghum results in higher weight loss when compared to torrefaction of Mesquite and Juniper wood. However at 300°C the weight loss of all three biomasses is generally the

same. The effect of varying the purge gas upon the weight loss of Sorghum can be seen in the thermograms comparing both Argon and Carbon-dioxide to Nitrogen, shown in Fig. 4.14 and Fig. 4.15.

A trend of increased weight loss when Carbon-dioxide was used as the purge gas observed for Mesquite wood and Juniper wood. This same trend is observed with Sorghum; however, the difference in mass loss between Nitrogen and Carbon-dioxide is much less significant for sorghum. Carbon-dioxide does consistently cause a higher amount of weight loss, but to a lesser extent when compared to Mesquite and Juniper due to the higher ash content of Sorghum.

As with previous experiment with Mesquite and Juniper there appears to be little difference in mass loss between samples using Nitrogen and Argon as the purge gas. These slight differences in mass loss are attributed to slight variations in the samples tested.

Comparing the active pyrolysis zone of Sorghum, Mesquite and Juniper shows that there is little difference in the temperature range over which active pyrolysis of Mesquite and Juniper occurs. However, the temperature range for the active pyrolysis zone of Sorghum is slightly smaller, ending near 350°C (compared to ~ 400°C for juniper and mesquite), suggesting that the hemicellulose and cellulose fractions of Sorghum may be more reactive than those of Mesquite and Juniper.

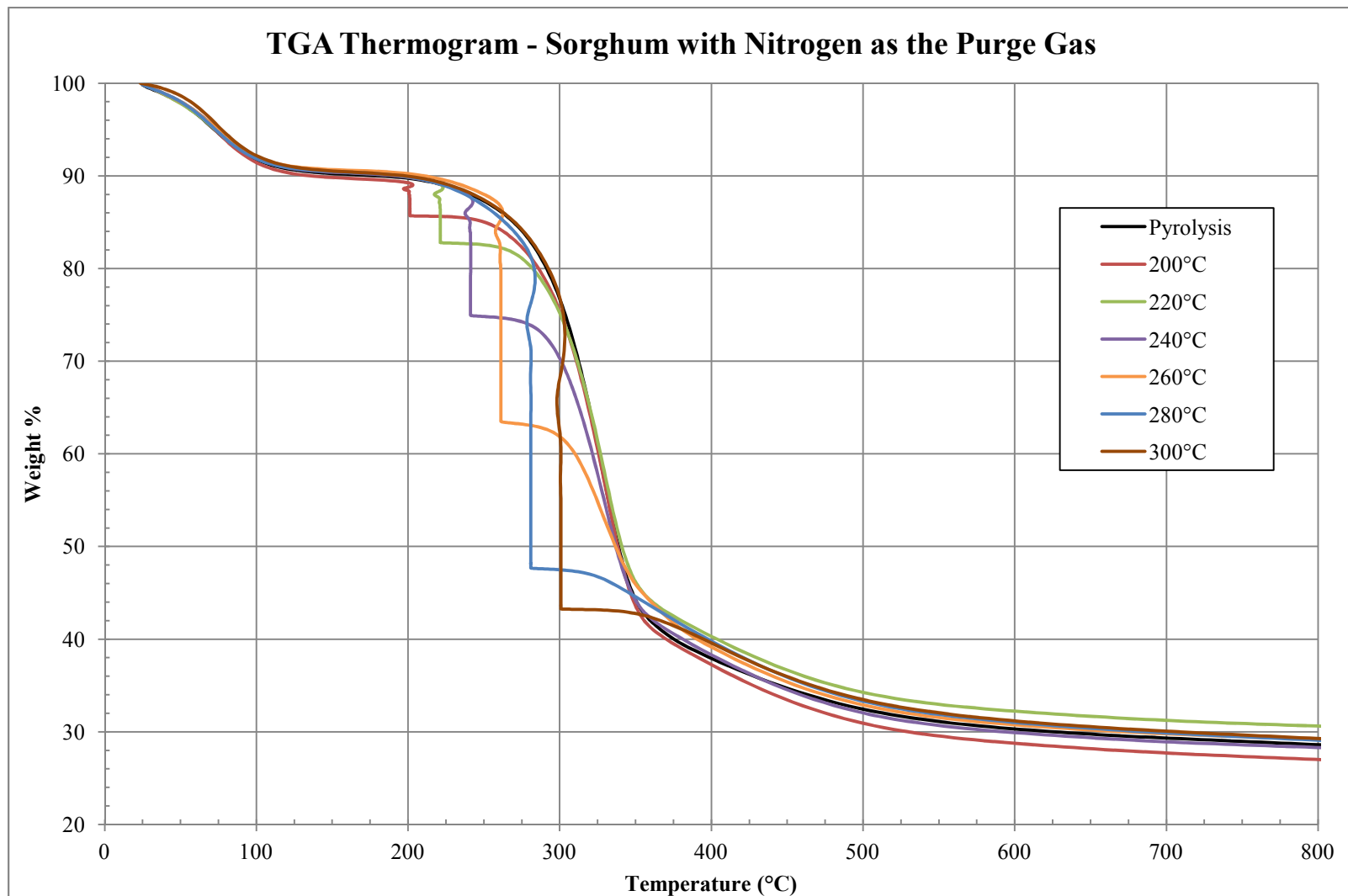


Fig. 4.11 - TGA thermograms of Sorghum pyrolysis and torrefaction using N₂ as the purge gas.

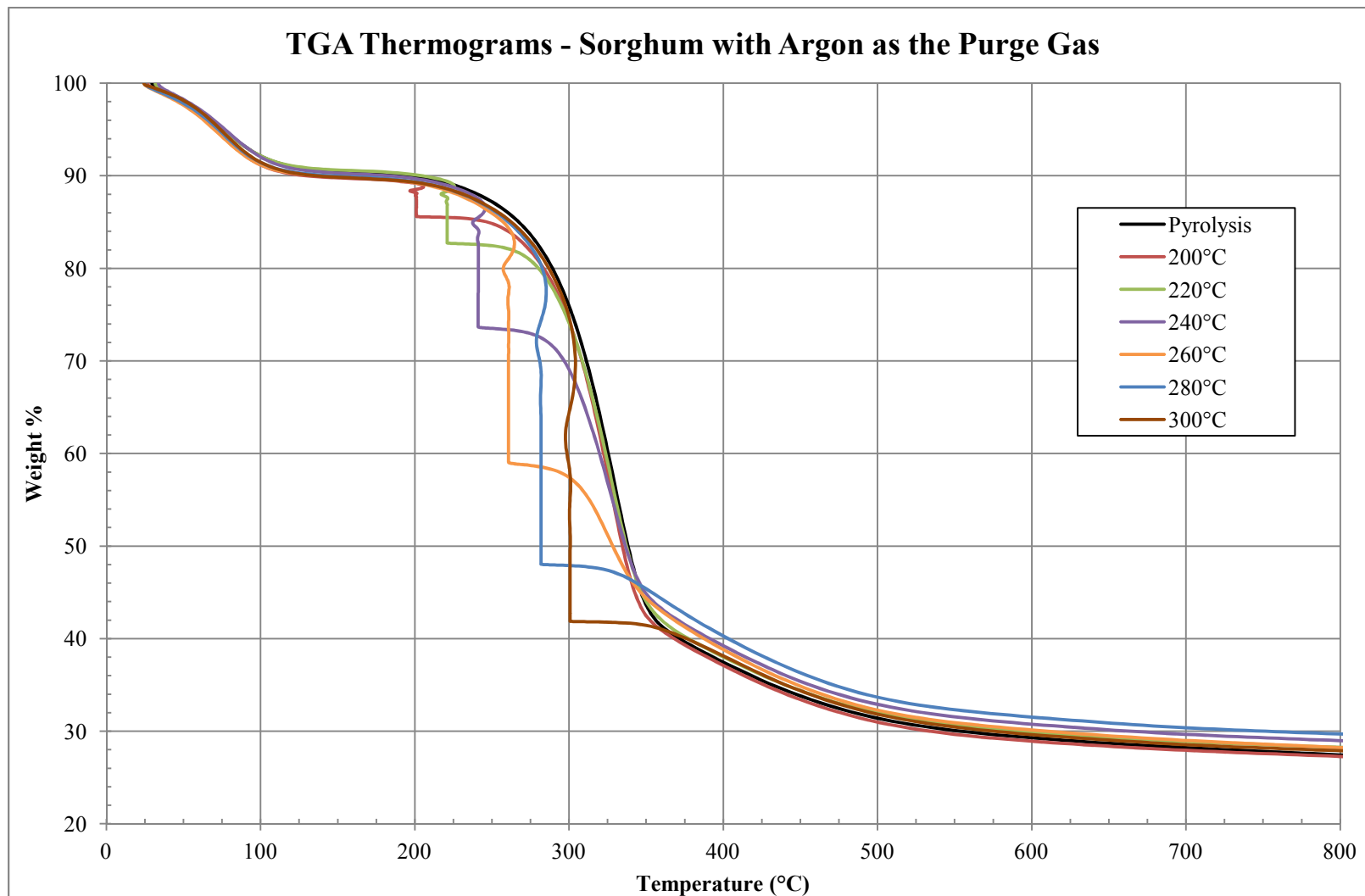


Fig. 4.12 - TGA thermograms of Sorghum pyrolysis and torrefaction using Ar as the purge gas.

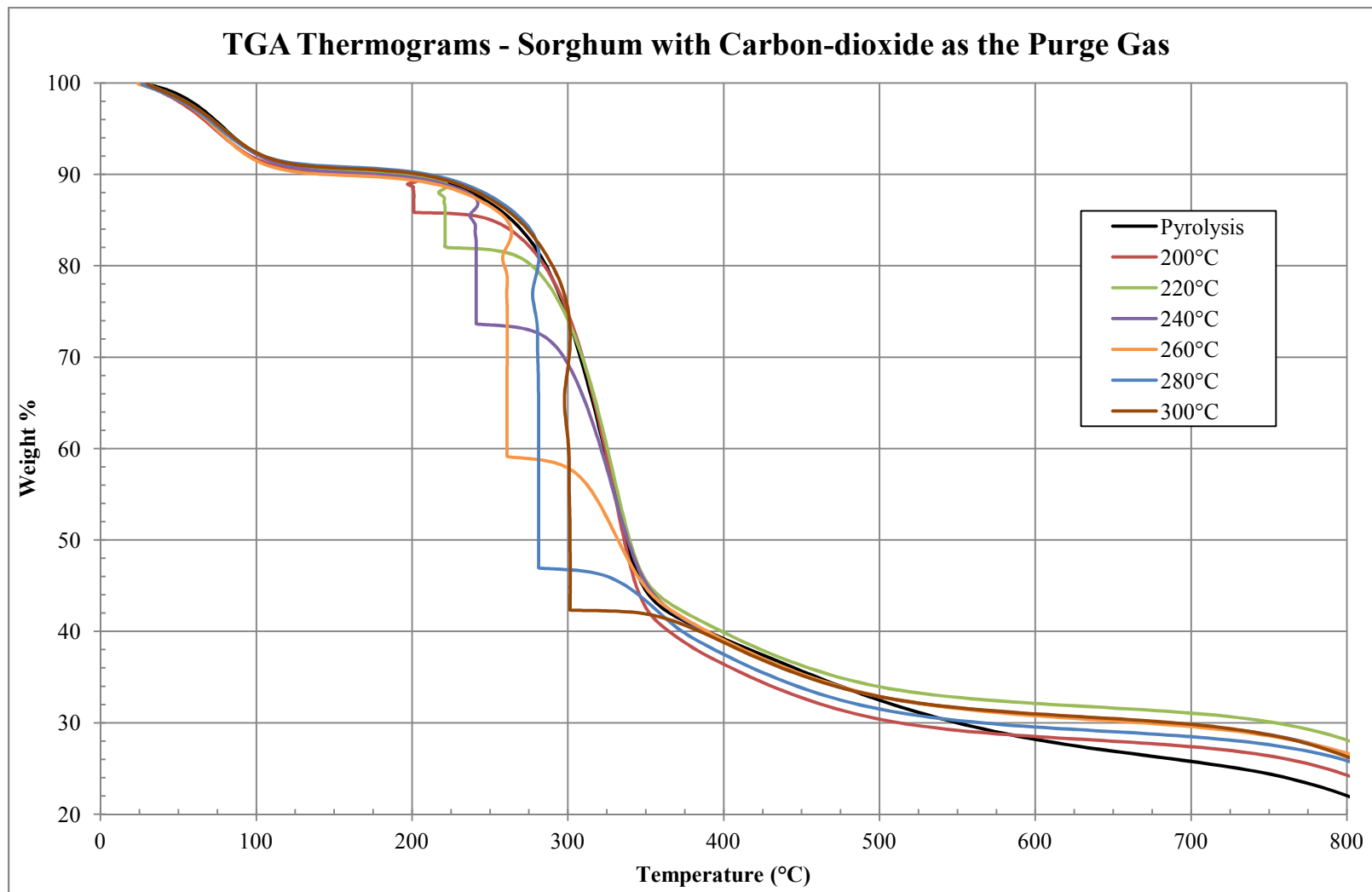


Fig. 4.13 - TGA thermograms of Sorghum pyrolysis and torrefaction using CO₂ as the purge gas.

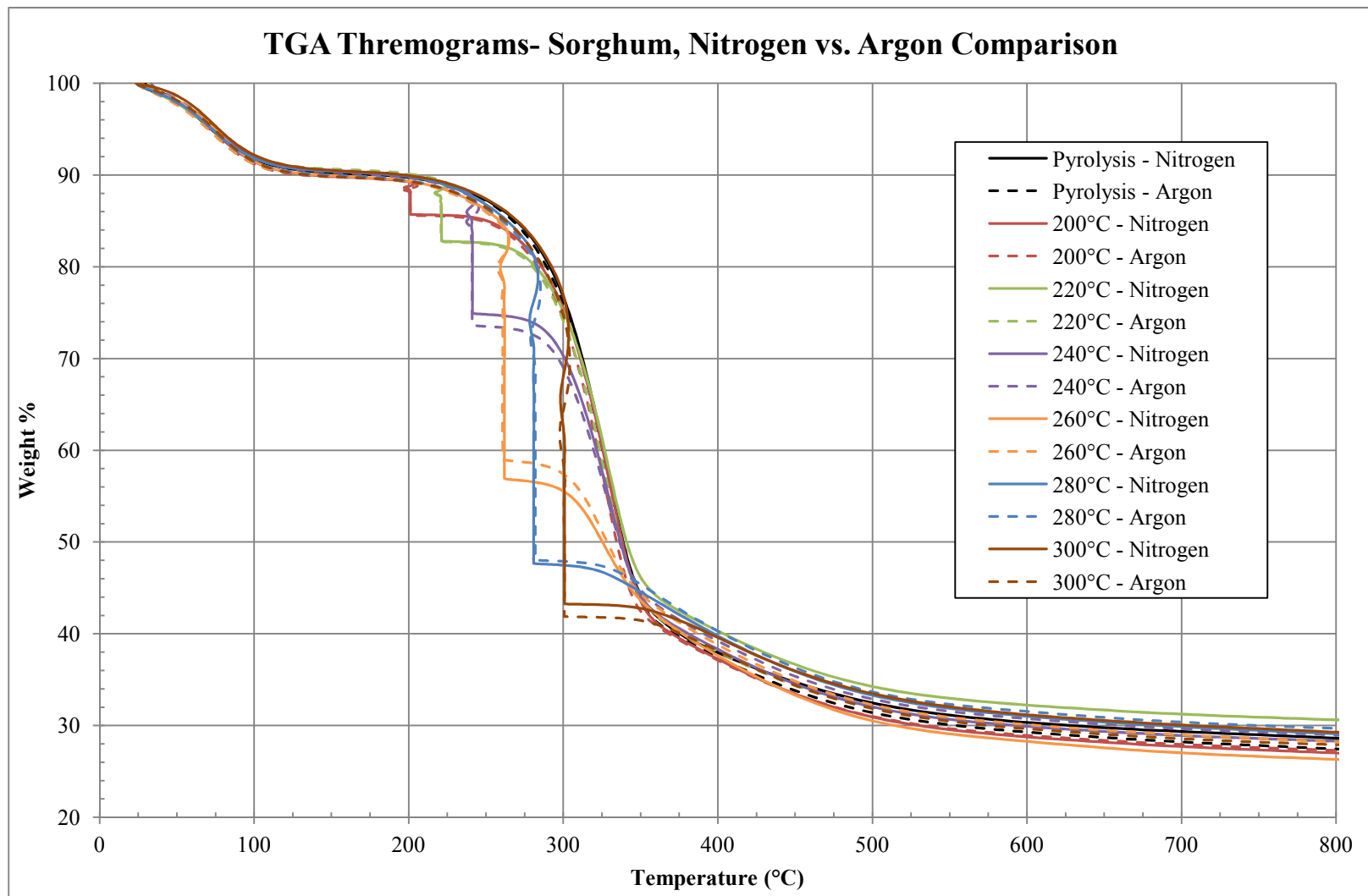


Fig. 4.14 - Comparison of thermograms from pyrolysis and torrefaction of Sorghum using N₂ and Ar as the purge gas.

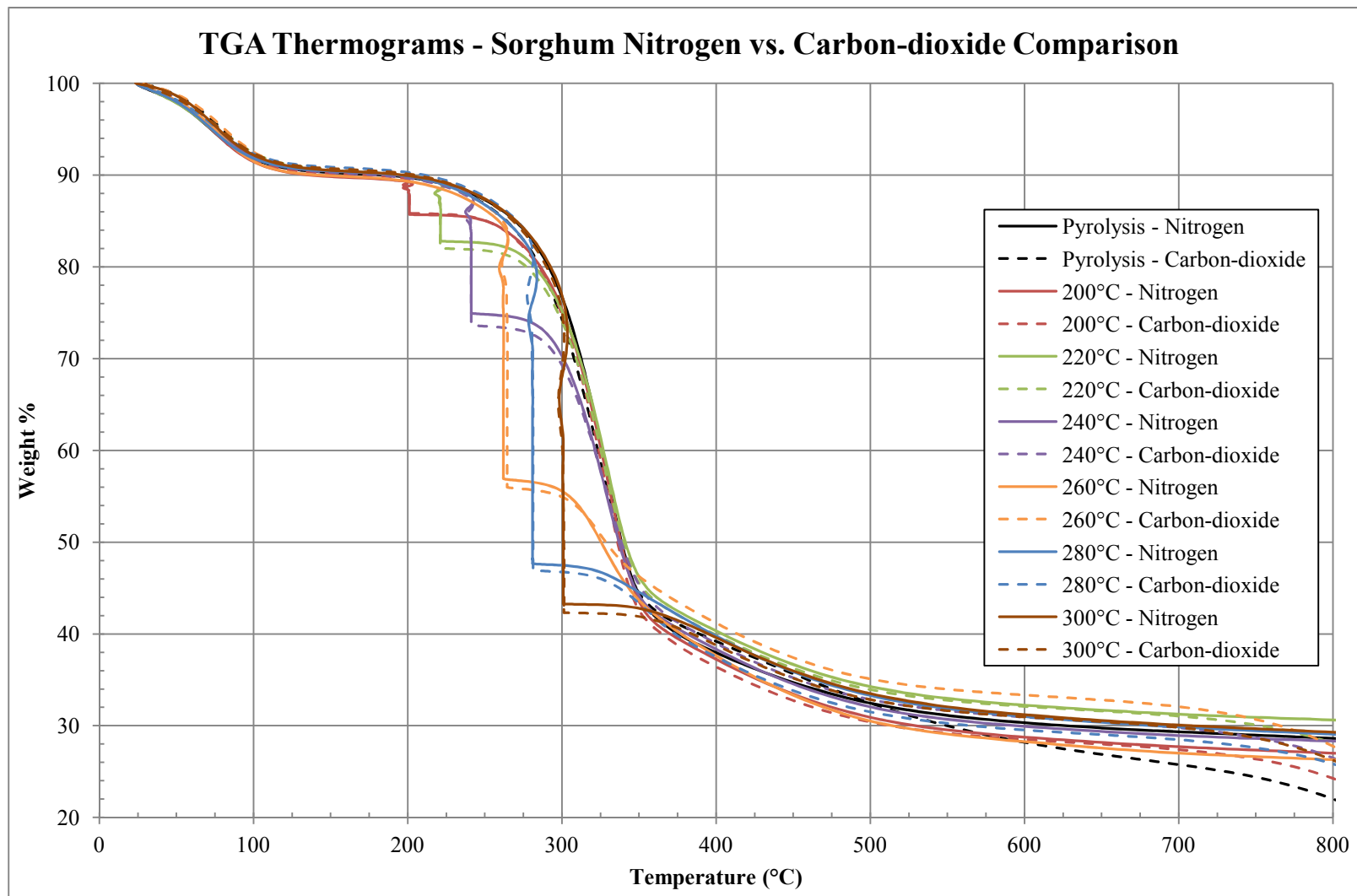


Fig. 4.15 - Comparison of thermograms from pyrolysis and torrefaction of Sorghum using N₂ and CO₂ as the purge gas.

4.4 DTG Analysis

DTG plots for each biomass and each purge gas will be presented in this section. General trends observed from analysis of DTG plots will be discussed. In depth discussion and formal conclusions will be presented after both the TGA and DTG results have been discussed in detail.

4.4.1 *Mesquite*

DTG analysis was carried out using the TA Q600 instrument. Analysis was done using the detailed procedure outlined in section 3.2.2 of this thesis. All of the biomasses were tested on an as received basis. As with the TGA thermograms in section 0 the DTG distributions for each torrefaction temperature have been overlaid on the same plot. The DTG curves for Mesquite pyrolysis and torrefaction using N₂, Ar, and CO₂ as the purge gas can be seen in Fig. 4.16, Fig. 4.17, and Fig. 4.18 respectively.

The DTG plots of mesquite wood pyrolysis and torrefaction shows the breakdown of hemicelluloses, cellulose, and lignin as described in section 3.3.2 of this thesis. The initial peak around 75°C shows the peak amount of mass lost due to drying of the raw biomass sample. The second peak near 275°C is the result of peak breakdown of hemicelluloses in the Mesquite wood.

As torrefaction temperature increases this peak becomes less pronounced resulting from the hemicelluloses within the Mesquite wood breaking down during torrefaction. It follows that as the torrefaction temperature increases more hemicellulose breaks down.

As the torrefaction temperature increases beyond 240°C a decrease in the peak cellulose breakdown is observed indicating that torrefaction at temperatures beyond 240-250°C results in breakdown of the celluloses contained within the biomass. As seen with the hemicelluloses peak, further increasing the torrefaction temperature results in further breakdown of cellulose during torrefaction.

There is a small but noticeable peak near 500°C shown on the DTG plots. This peak is a result of lignin decomposition. Due to lignin's rather large decomposition temperature range (when compared to hemicelluloses and cellulose), the peak of lignin decomposition is rather small.

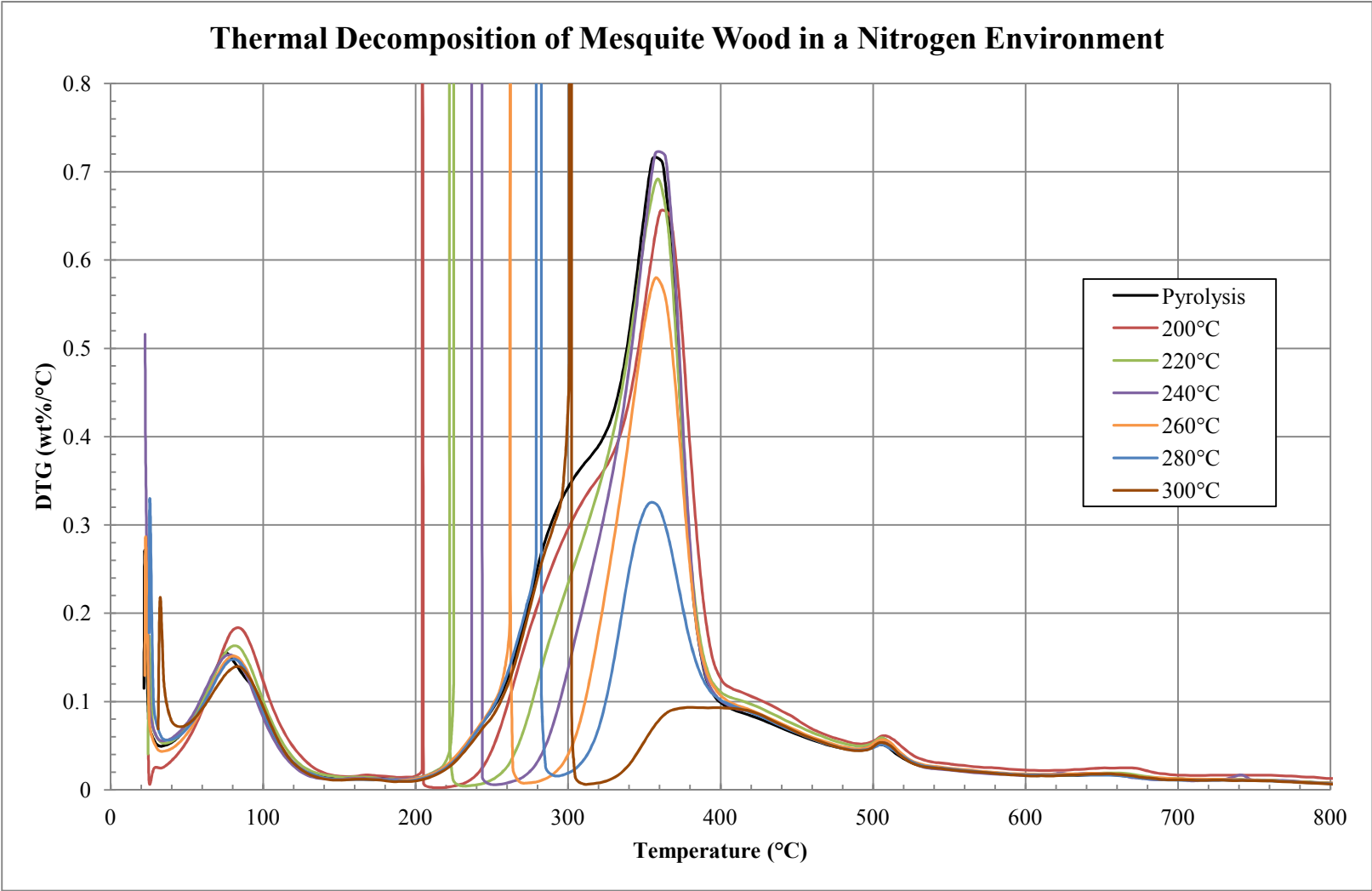


Fig. 4.16- DTG distribution of Mesquite wood pyrolysis and torrefaction using N₂ as the purge gas.

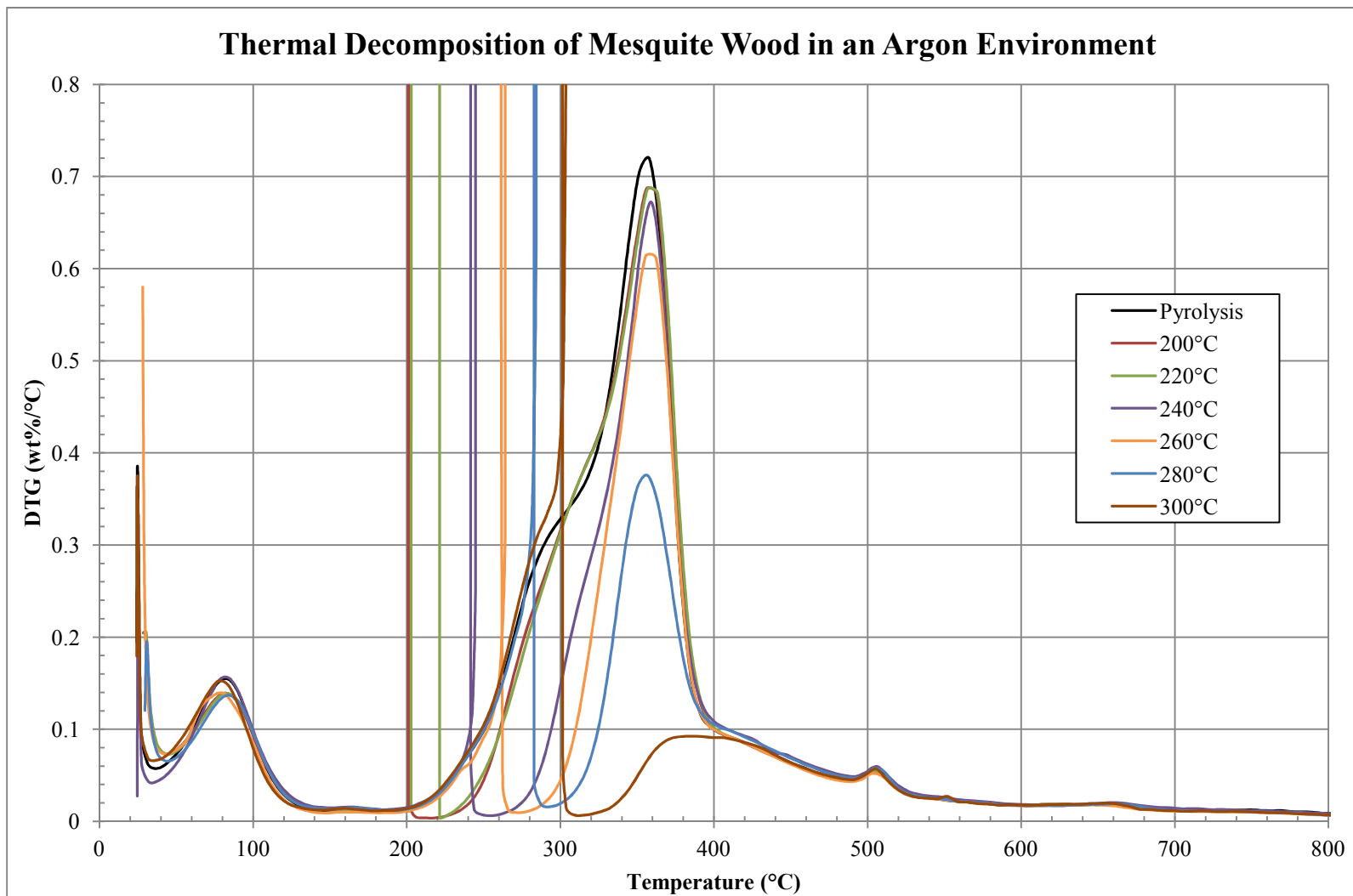


Fig. 4.17 – DTG distribution of Mesquite wood pyrolysis and torrefaction using Ar as the purge gas.

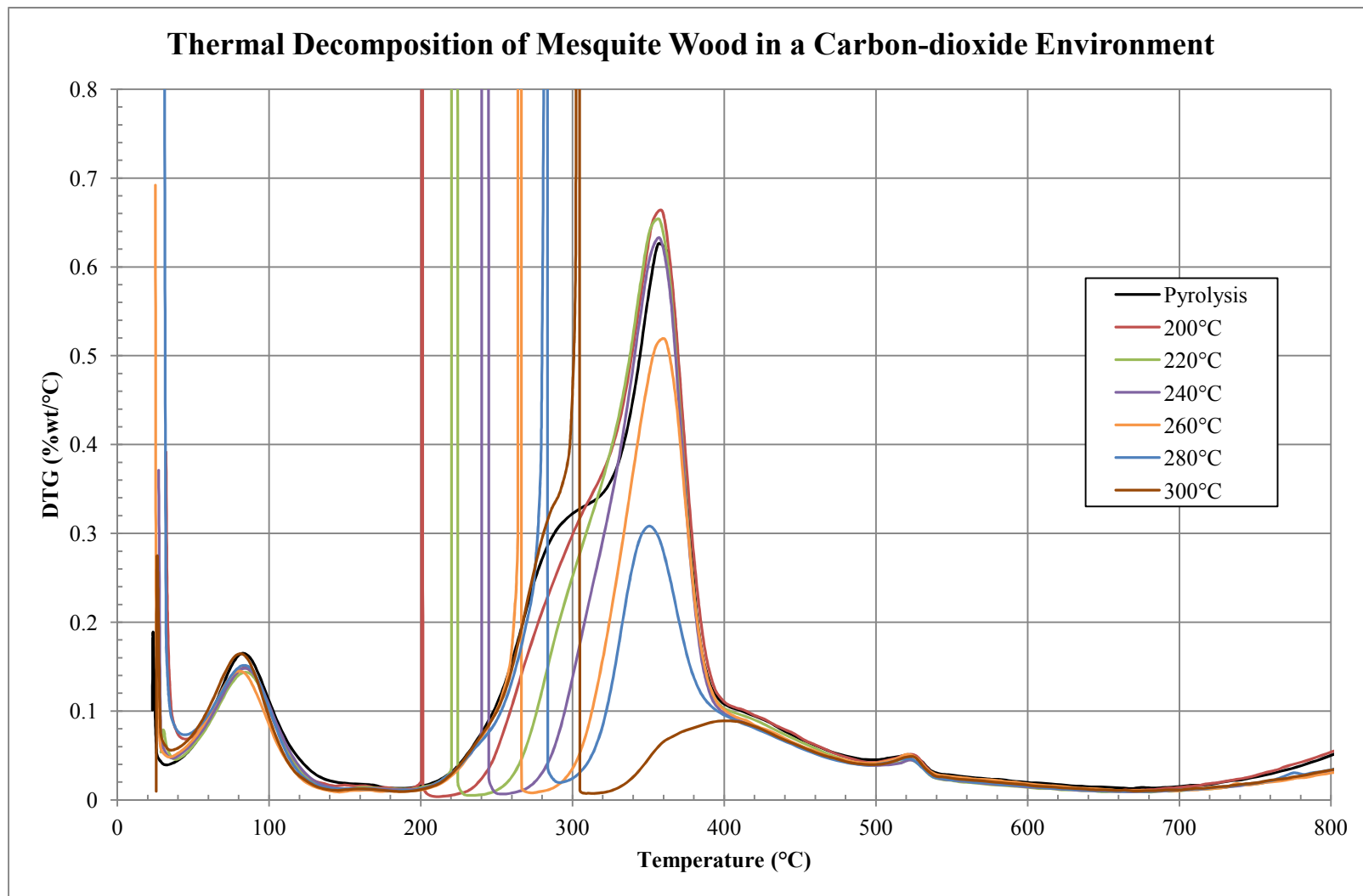


Fig. 4.18 – DTG distribution of Mesquite wood pyrolysis and torrefaction using CO₂ as the purge gas.

When comparing the results obtained from all three purge gasses there appears to be no discernable difference between the results for Nitrogen and Argon. This analysis coincides with the results of comparison of TGA thermograms when using Nitrogen and Argon as purge gasses. However, comparison of the DTG plots when using Nitrogen and Carbon-Dioxide shows differences in thermal breakdown of the biomass depending on the purge gas used with the most noticeable difference being a decrease in the peak of cellulose breakdown (350°C) when CO₂ was used as the purge gas. There is also a noticeable shift in the peak lignin decomposition to a slightly higher temperature when using Carbon-dioxide as the purge gas.

4.4.2 *Juniper*

DTG analysis of Juniper pyrolysis and torrefaction was done in the same manner as before. Using data obtained from the TA Q600 instrument, DTG distributions for each purge gas were created. The DTG distributions of Juniper using Nitrogen, Argon, and Carbon-dioxide as the purge gas can be seen in Fig. 4.19, Fig. 4.20, and Fig. 4.21 respectively.

The DTG distribution of Juniper has the same appearance as the DTG distribution of Mesquite, the initial peak representative of the drying of the raw biomass and the resulting mass loss being entirely moisture. The peak of hemicellulose decomposition in Juniper is not as pronounced when compared to that of Mesquite. This is mostly due to the hemicellulose in Mesquite being more reactive than the hemicellulose in Juniper as previously stated. The peak of cellulose breakdown in Juniper occurs at roughly 375°C, a slightly higher temperature than the peak of cellulose breakdown in Mesquite (~350°C).

The peak of cellulose breakdown is also slightly larger for Juniper, meaning that the breakdown of cellulose in Juniper occurs more rapidly than the breakdown of cellulose in Mesquite. This suggests that although the hemicellulose in Juniper is less reactive than the hemicellulose in Mesquite, the cellulose fraction of Juniper wood is more reactive than the cellulose found in Mesquite wood.

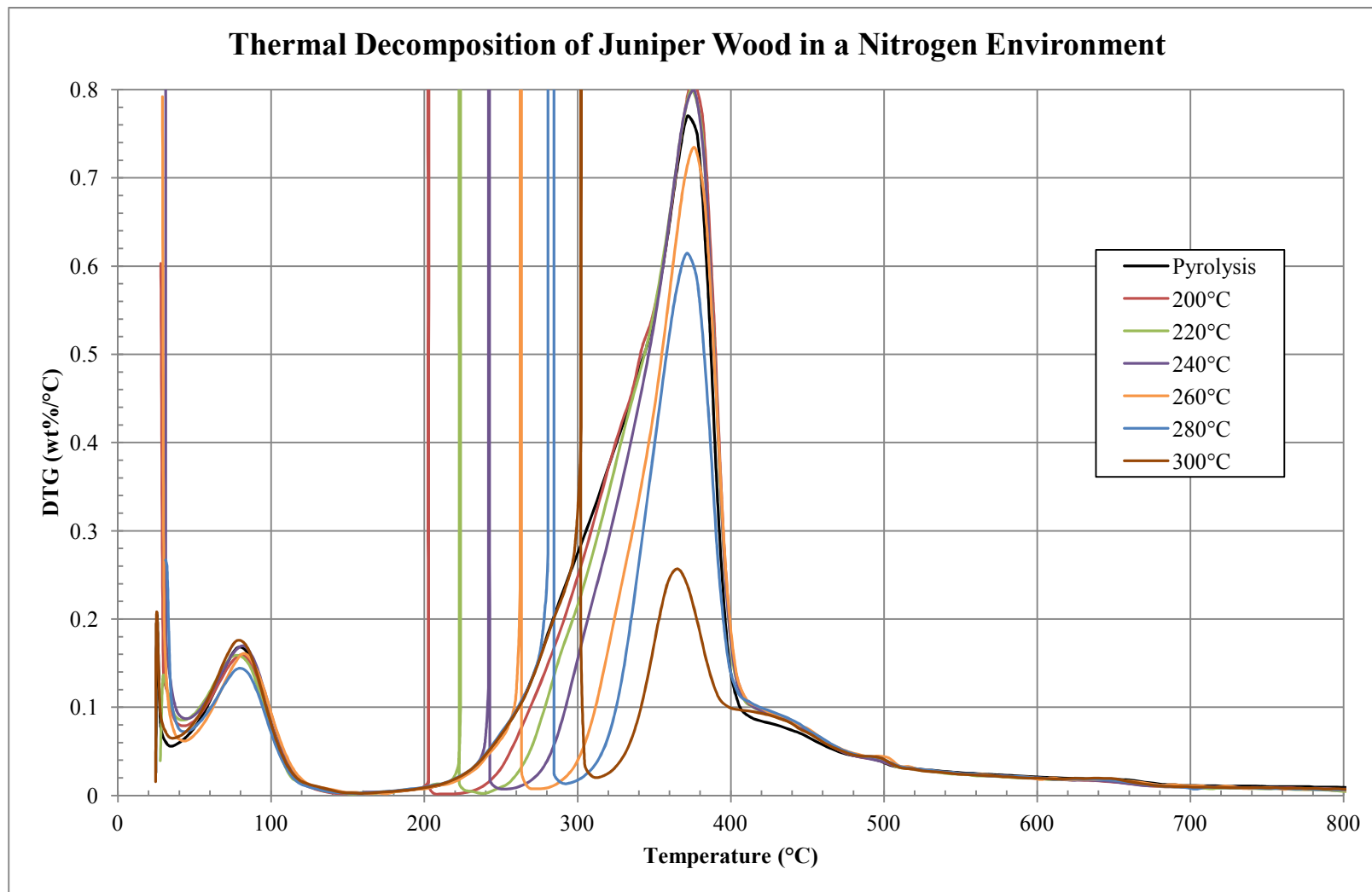


Fig. 4.19 – DTG distribution of Juniper wood pyrolysis and torrefaction using N₂ as the purge gas.

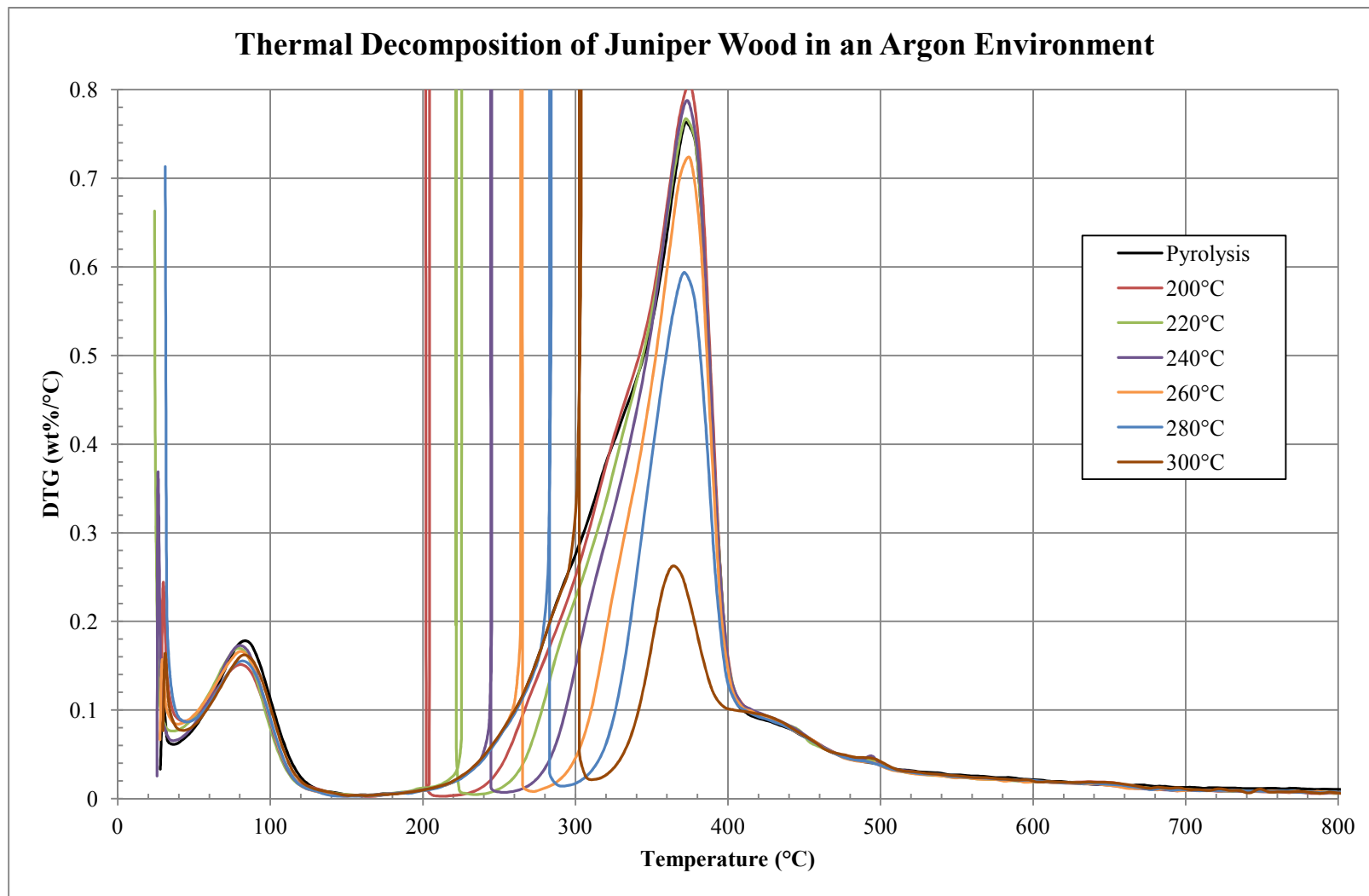


Fig. 4.20 – DTG distribution of Juniper wood pyrolysis and torrefaction using Ar as the purge gas.

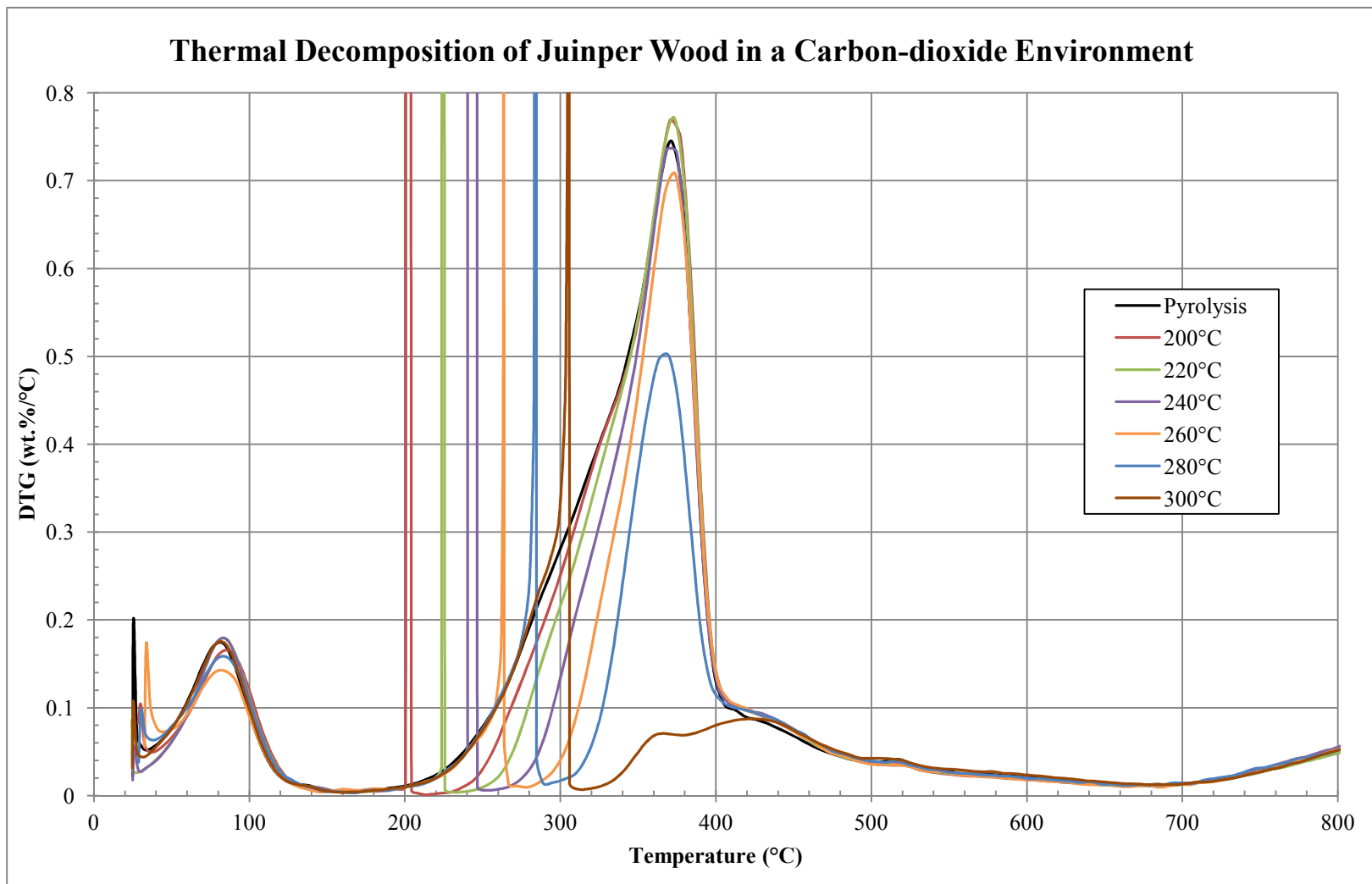


Fig. 4.21 – DTG distribution of Juniper wood pyrolysis and torrefaction using CO₂ as the purge gas.

It is also interesting to note that for both Mesquite and Juniper (as well as sorghum which will be shown and discussed later) the breakdown of cellulose appears to end either at 400°C or slightly after. This point on the DTG distributions coincides with the change of slope on the TGA thermograms presented in section 3.3.1, which was previously defined as the point when the active pyrolysis zone ends and the passive pyrolysis zone begins. Plotting the TGA thermogram and DTG distribution of pyrolysis of Juniper with Nitrogen as the purge gas clearly shows this observation. Based upon this it can be stated that hemicellulose and cellulose decomposition occurs entirely in the active pyrolysis zone, and that reactions in the passive pyrolysis zone can be attributed solely to lignin decomposition and further evolution of volatile matter.

From the DTG distributions of Juniper the peak lignin decomposition appears less pronounced than the peak of lignin decomposition seen on the DTG distributions of Mesquite. However, it is seen that lignin breakdown continues to occur at higher temperatures in Juniper. A slight peak in lignin decomposition can be seen near 500°C for Juniper.

As with Mesquite wood, the DTG distributions of Juniper using Nitrogen and Argon as the purge gas show very little difference. The peak of hemicellulose, cellulose, and lignin decomposition occurs at the same temperature for both gasses. Comparison of the DTG distributions of Juniper wood using Nitrogen and Carbon-dioxide as the purge gas shows the same trends observed for mesquite wood. Carbon-dioxide appears to cause the peak of cellulose breakdown to be smaller than that of torrefaction in a Nitrogen atmosphere. The shift in the lignin peak observed with Mesquite torrefaction in a Carbon-dioxide environment is also apparent with the torrefaction of juniper in a Carbon-dioxide environment.

4.4.3 *Sorghum*

DTG analysis of Sorghum pyrolysis and torrefaction was done using the same method as previous experiments with Mesquite and Juniper. Using data obtained from the TA Q600 instrument, DTG distributions for each purge gas were created. The DTG distributions of Sorghum using Nitrogen, Argon, and Carbon-dioxide as the purge gas can be seen in Fig. 4.22, Fig. 4.23, and Fig. 4.24 respectively.

The DTG distribution of the torrefaction and pyrolysis of Sorghum have the same general shape as previous experiments with Mesquite and Juniper. The peak of hemicellulose breakdown for

Sorghum appears almost non-existent, suggesting that the hemicellulose fraction of Sorghum is less than both Mesquite and Juniper. The peak of cellulose breakdown also occurs at a noticeably lower temperature than that of Mesquite and Juniper and is also larger than both of the other biomasses tested. This suggests that the cellulose fraction of Sorghum is more reactive than the cellulose fraction of both Mesquite and Juniper. The slight lignin peaks observed with both Juniper and Mesquite do not appear on the DTG distribution of sorghum. The absence of this peak implies that the lignin fraction of Sorghum has a more gradual breakdown than the lignin fraction of Mesquite and Juniper. Looking at the DTG curves for the torrefaction of Sorghum at 280°C and 300°C shows that torrefaction at these temperatures results in nearly the entire cellulose and hemicellulose fractions breaking down. Unlike what was observed from torrefaction of Juniper and Mesquite, torrefaction of Sorghum at 240°C does have a noticeable effect upon the cellulose peak.

Similar results to those seen when looking at the effect of Argon and Carbon-dioxide on Mesquite and Juniper can be seen when comparing the DTG distributions of Sorghum with each purge gas. There are very slight variations between the DTG distributions from experiments run with Nitrogen and Argon as the purge gas. Also, as previously observed, using Carbon-dioxide as the purge gas resulted in the peak of cellulose breakdown being smaller. The effect of Carbon-dioxide on the lignin peak cannot be determined due to no peak for lignin breakdown being visible on the DTG distributions of Sorghum.

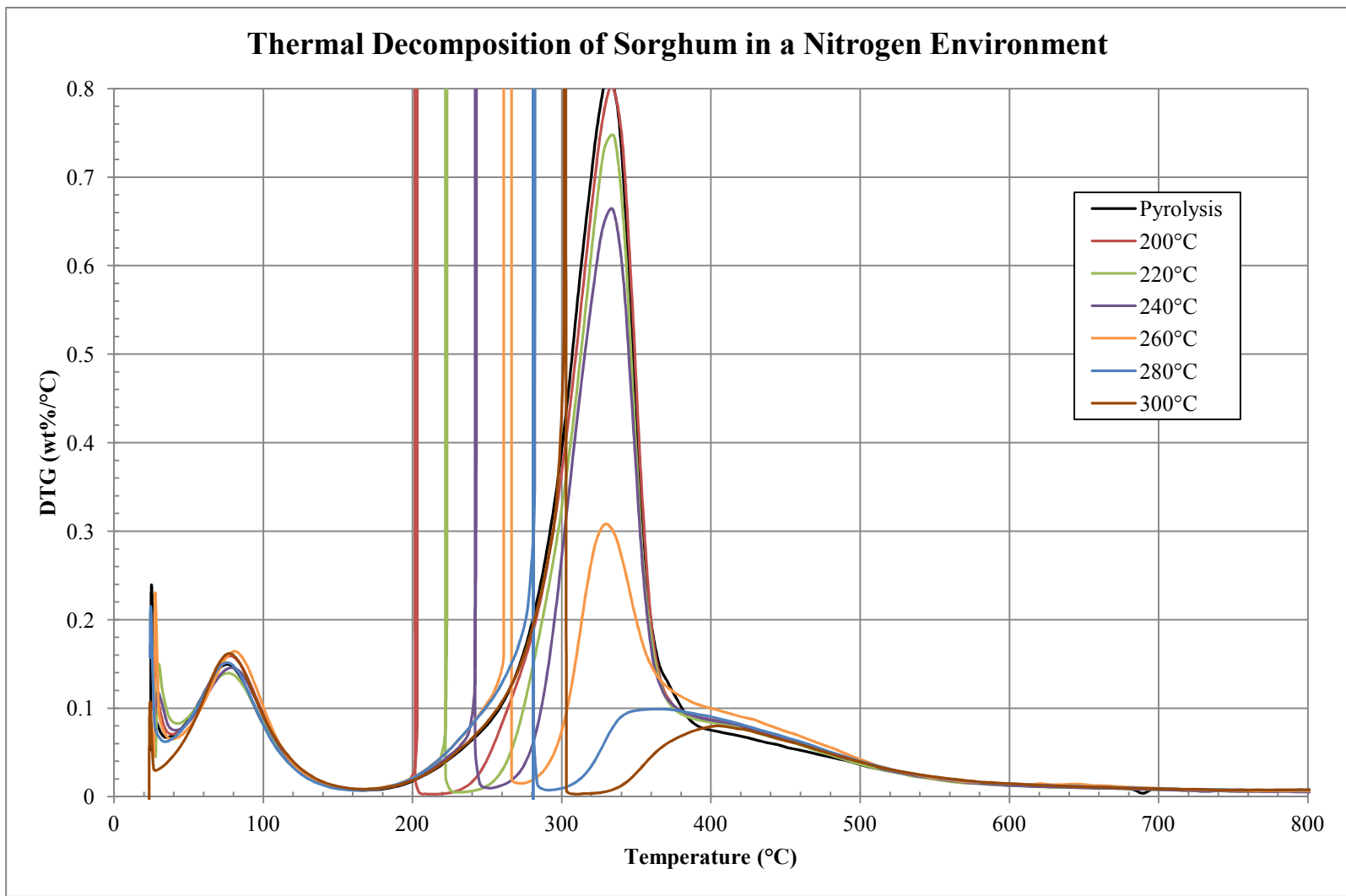


Fig. 4.22 - DTG distribution of Sorghum pyrolysis and torrefaction using N₂ as the purge gas.

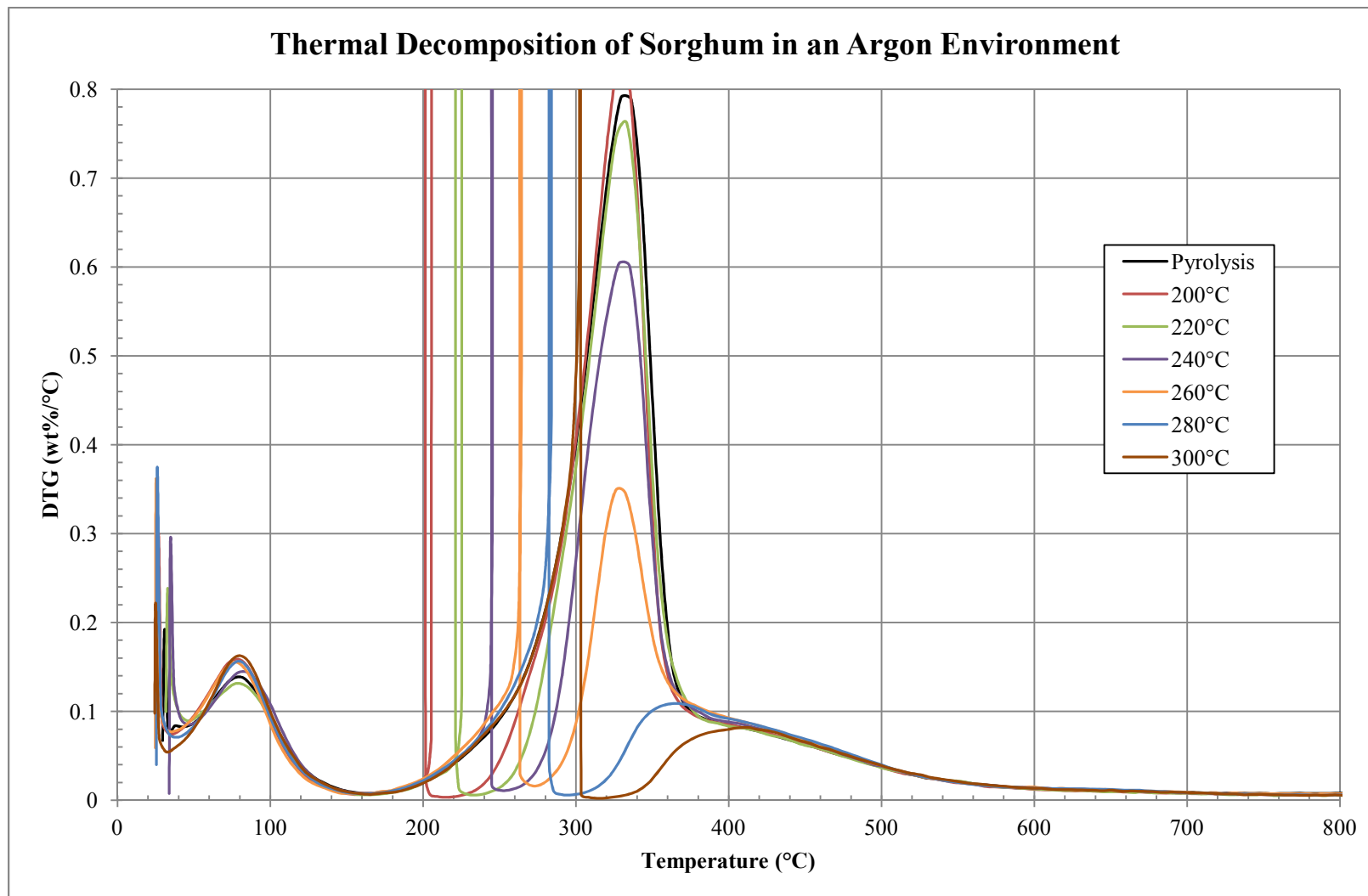


Fig. 4.23 - DTG distribution of Sorghum pyrolysis and torrefaction using Ar as the purge gas.

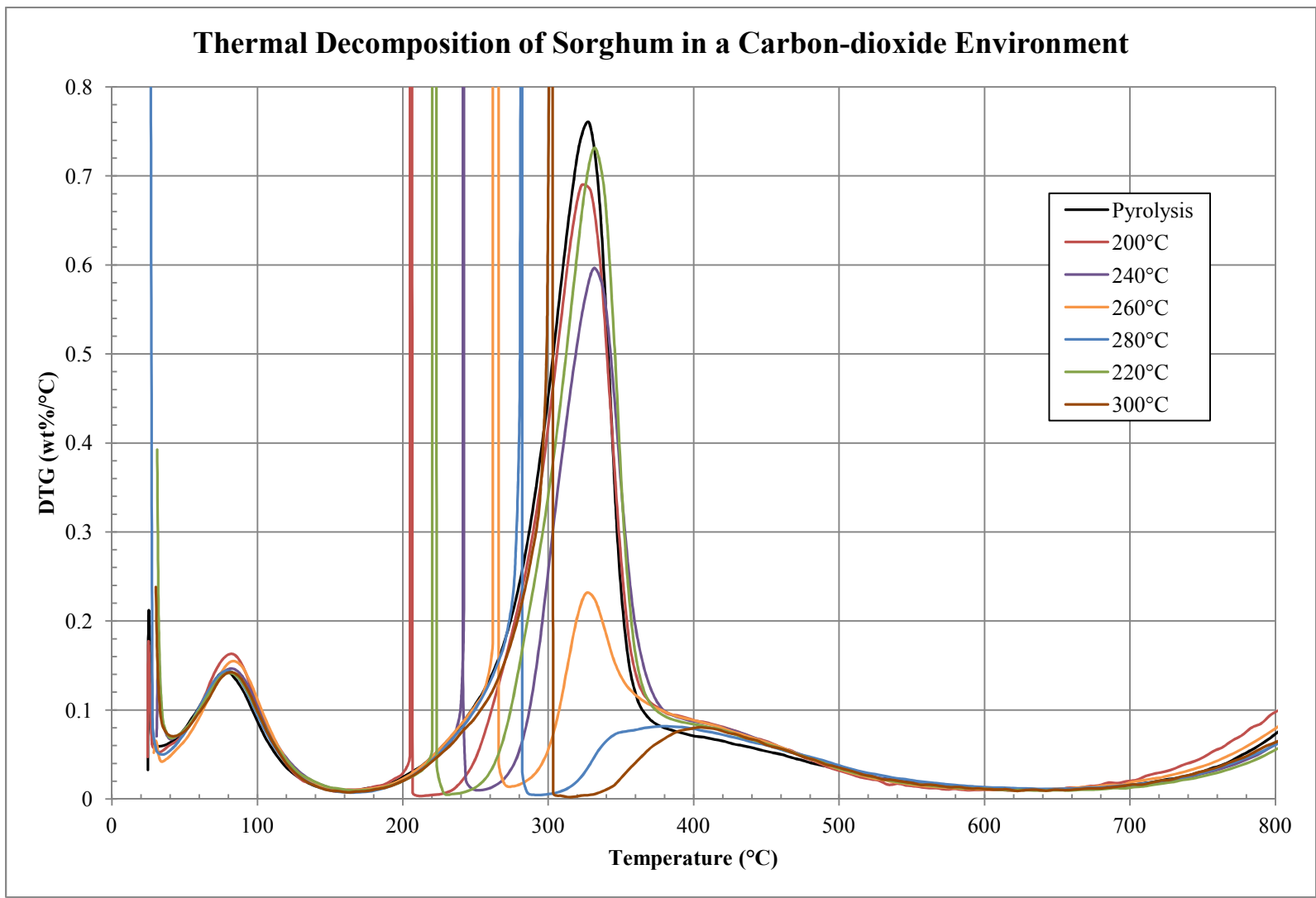


Fig. 4.24 - DTG distribution of Sorghum pyrolysis and torrefaction using CO₂ as the purge gas.

4.5 TGA/DTG Discussion and Hypotheses

Based upon the analysis of the data obtained there are several trends that can be observed. From the DTG distributions it can be seen that as the torrefaction temperature increases the peak of hemicellulose and cellulose breakdown becomes smaller, meaning the reaction rate of is decreases with increasing torrefaction temperatures. This is a directly related to mass lost due to the liberation of light weight volatiles during the torrefaction process. Previous researchers [9] have used the Arrhenius law as the basis for kinetic modeling of torrefaction. In general, if we assume a first order reaction, a relationship between reaction rate (dm/dT) and the mass of volatiles (m_v) can be drawn from the Arrhenius law:

$$\frac{dm}{dT} \propto m_v \quad (4)$$

Therefore, as more volatiles are liberated at higher torrefaction temperatures (seen in the thermograms as more weight loss) the rate at which volatiles will be released will be smaller. There is no noticeable drop in the peak value of lignin breakdown as torrefaction temperature is increased. Due to the complex structure of lignin and the wide temperature range over which lignin breaks down this result is not surprising.

Further analysis of both the TGA thermograms shows an increased amount of weight loss when Carbon-dioxide is used as the torrefaction medium when compared to the results of using Nitrogen and Argon as the purge gas. As previously stated, the weight loss results of biomass torrefied with Nitrogen and Argon are very similar with slight variations, and it can be assumed that both Nitrogen and Argon have the same effect when used as a torrefaction medium. This conclusion appears to rule out the possibility of thermal-fluid properties (molecular weight, specific heats, etc.) as the cause of increased weight loss with CO₂, as the properties of Nitrogen and Argon are different yet produce similar results (Fig. 4.25).

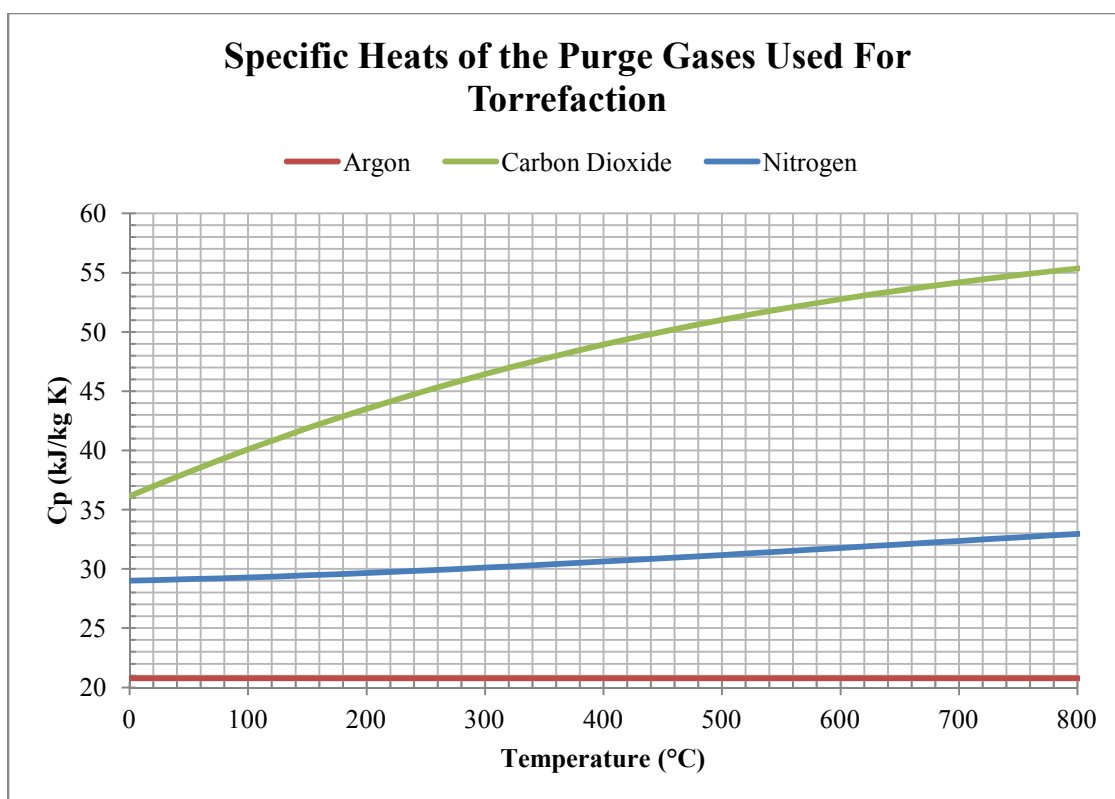
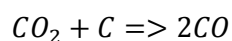


Fig. 4.25 – Specific heat values of the purge gases used during experimentation over a wide temperature range.

Both Nitrogen and Argon are inert gasses below 1000°C, a temperature well above the range over which torrefaction was done (200-300°C). However, Carbon-dioxide can react with fixed carbon at temperatures below 1000°C to form Carbon-monoxide as given by the Boudouard reaction:



The Boudouard reaction has been used to explain the production Carbon-monoxide from biomass gasification when CO₂ is used as the gasification medium.[4] At higher temperatures, such as those used in gasification, the reaction readily occurs (Fig. 4.26).

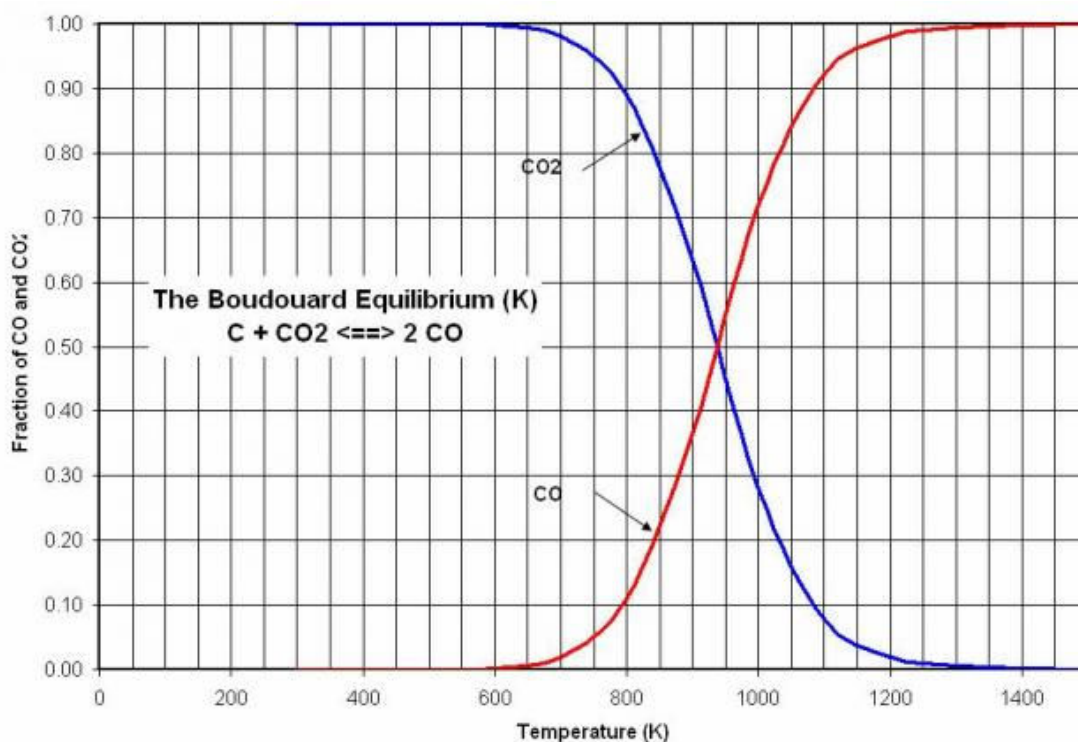


Fig. 4.26 - The Boudouard reaction over a wide temperature range. [24]

In the case of the experiments done in this thesis, during torrefaction the fixed carbon present in the biomass could have reacted with the CO₂ that was used as a purge gas. This reaction would result in more volatiles being liberated and therefore a larger amount of mass loss when using CO₂ as the purge gas during torrefaction. Below 800°C the reaction is dominated by Carbon-dioxide and the amount of Carbon-monoxide produced is minimal. For the temperature range in which torrefaction was done (200-300°C) the amount of CO produced as a result of the reaction is very small (>0.5% by mass). However, given the long residence time (one hour) the amount of mass lost due to this reaction could become significant. It should be noted that the Boudouard reaction is readily seen on some on the DTG distributions of Carbon-dioxide as the purge gas at the tail end of the distributions (temperature > 700°C) where the curve begins to increase indicating that a reaction is occurring.

The results from the TGA thermograms of Sorghum are different than the results for Mesquite and Juniper. As stated before this is mostly due to the difference in chemical composition between the biomass, given that Mesquite and Juniper are woods and Sorghum is a grass. It is

apparent however that the effect of using CO₂ is less significant for Sorghum. The high ash content of Sorghum (9.62%) compared to Mesquite (1.67%) and Juniper (1.91%) is the most likely cause. The ash contained within the biomass will inhibit the reaction of CO₂ with fixed carbon, with the end result being more closely related amount of weight loss for all three purge gasses when torrefying Sorghum.

Further analysis of the data obtained from TGA experimentation shows that the fluid properties of the purge gases may have some effect upon both the DTG distributions and TGA thermograms. The heater power required to maintain the isothermal torrefaction temperature varies depending upon the purge gas used (Table 4.3).

Table 4.3 – Average heater power required to maintain 240°C temperature during the torrefaction of juniper wood.

Purge Gas	Avg. Heater Power (μv)
Nitrogen	27.74
Argon	21.52
Carbon- Dioxide	41.84

The trends observed from the DTG and TGA analysis are most likely due to a combination of thermal properties and chemical reaction. As stated before, no previous research has been found that investigated the effect of different purge gases upon the torrefaction of biomass. Therefore, it is difficult to form a concrete hypothesis based upon the results of this research alone. Each experiment has been done at least twice to verify the validity of the results. Any future research on torrefaction of biomass with Carbon-dioxide as the purge gas should first determine if the trends observed from this research are in fact correct, and secondly investigate further the cause of the trends observed.

4.6 Determination of Optimal Torrefaction Temperature

Based upon the TGA thermograms and DTG distributions of all three biomasses using each of the three purge gasses an optimal torrefaction temperature can be determined. From the TGA thermograms presented for each biomass and purge gas at 240°C more than 70% of the initial mass of the biomass remains after torrefaction. This is independent of both biomass and purge

gas. Tests conducted at a torrefaction temperature of 260°C resulted in roughly 58-65% of the biomass remaining. DTG distributions for all three biomass show that torrefaction temperatures above 240°C results in a drop in the peak cellulose breakdown. This implies that torrefaction at temperatures above 240°C causes breakdown of the cellulose contained within the biomass to occur during torrefaction.

Furthermore an estimated percent of energy retained after torrefaction can be calculated based upon the raw biomass fuel properties and the TGA weight traces. The energy retention estimates were calculated based upon the HHV of the fuel on a dry ash-free (DAF) basis and the amount of fixed carbon (FC) and volatile matter (VM) in the biomass. If we use the DAF HHV of the biomass, the energy content comes entirely from the VM and FC and the following relation can be used [5]:

$$HHV_{DAF} \left(\frac{kJ}{Kg} \right) = HHV_{VM} * VM + HHV_{FC} * FC \quad (5)$$

If we assume that the mass lost during torrefaction is entirely due to liberation of volatiles than the HHV of the torrefied biomass can be estimated:

$$HHV_{DAF,TB} \left(\frac{kJ}{Kg} \right) = (wt\% * VM * HHV_{VM}) + (HHV_{FC} * FC) \quad (6)$$

where wt% represents the weight remaining after torrefaction. Although it is hypothesized that the larger amount of weight loss when CO₂ is used as the torrefaction medium is due to the reaction of CO₂ with fixed carbon (and therefore the mass of FC will drop during torrefaction) the same estimation can still be used.

Using the estimation proposed above to determine the HHV of the torrefied biomass on a DAF basis it is possible to estimate the amount of energy retained after torrefaction. Although, the HHV of the torrefied biomass is larger there is an inherent mass loss due to the torrefaction process, therefore, the amount of energy retained as a result of the torrefaction process can be calculated:

$$Energy\ Retained\ (\%) = \frac{M_{TB} * HHV_{TB}}{M_{RB} * HHV_{RB}} * 100 \quad (7)$$

Using data from the heat value analysis of the raw biomass, which gives the HHV of the VM, with the proximate analysis results an estimated HHV of the torrefied biomass can be calculated

and therefore an estimated energy retained %. The estimated values for energy retained for all three biomass and all three purge gases can be seen in Table 4.4.

Table 4.4 – Estimated energy retained for all three biomass and purge gases for the entire range of torrefaction temperatures.

Biomass	Temp					
	200	220	240	260	280	300
Mesquite - N ₂	93.01	90.66	86.77	80.88	65.87	56.19
Mesquite - Ar	94.10	91.27	85.38	80.88	70.54	58.39
Mesquite - CO ₂	93.56	90.66	84.66	77.64	65.70	51.64
Juniper - N ₂	94.25	92.55	88.82	82.77	73.32	56.42
Juniper - Ar	94.25	91.35	88.82	82.43	74.20	57.51
Juniper - CO ₂	93.69	91.35	86.10	81.66	68.70	57.51
Sorghum - N ₂	94.97	92.73	87.94	73.91	65.22	59.91
Sorghum - Ar	93.80	92.73	86.60	72.01	65.22	58.81
Sorghum - CO ₂	93.27	92.18	86.60	73.00	64.19	58.81

Based upon the mass loss observed from TGA thermograms as well as the estimated energy retention calculations the optimal torrefaction temperature was determined to be 240°C. For all of the biomass tested in each purge gas environment, torrefaction at 240°C results in over 85% energy retention as well as 70% of the initial mass remaining. From the DTG distributions it is also clear that torrefaction at 240°C resulted in the breakdown of hemicellulose with minimal to no impact upon the cellulose in the biomass. These results coincide with previous studies [8, 3] that have suggested 240°C as the optimal torrefaction temperature.

4.7 Torrefaction Using a Laboratory Oven

After determining the optimal torrefaction temperature large samples of each biomass were torrefied in a laboratory oven using Nitrogen, Argon, and Carbon-dioxide as the purge gas. Torrefaction was carried out as outlined in section 3.2.2.2 of this thesis. Torrefied samples were sent to Hazen Laboratories in Colorado for proximate, ultimate, and heat value analysis. The fuel properties of both the torrefied biomass can be seen in Table 4.5, Table 4.6, and Table 4.7.

Comparing the properties of raw biomass (seen in Table 4.1) and torrefied biomass the affect of torrefaction at 240°C upon the fuel properties of the biomass can be seen. As expected torrefaction of the raw biomass resulted in reduced moisture content in the biomass. However, Juniper wood torrefied in Carbon-dioxide is the only sample which did not see a decrease in moisture content possibly due to experimental error. Torrefaction of raw biomass also resulted in an increased ash and fixed carbon content for all biomass tested. The increase in ash and FC is mostly due to the decrease in moisture content and liberation of light weight volatiles during torrefaction.

Examination of ultimate analysis shows that, the Oxygen-Carbon (O/C) ratio decreased as a result of torrefaction. Decrease in the Hydrogen, Nitrogen, and Sulfur content of the fuel was also observed, although the decrease in Oxygen content was much more significant. The HHV of the fuel increased as a result of torrefaction with the HHV of sorghum increasing the most (~3500 kJ/kg). The increase in HHV is in direct relation to the decrease in Oxygen content.

Comparison of the properties of the biomass torrefied in different environments further demonstrates the effect different torrefaction mediums had upon fuel properties. Biomass torrefied in an Argon or Nitrogen environment exhibit little difference in fuel properties. However, the fuel properties of biomass torrefied in Carbon-dioxide are slightly different than those torrefied with Argon or Nitrogen. The biomass torrefied in Carbon-dioxide exhibited a smaller increase in fixed carbon content. Torrefaction of Juniper in a Carbon-dioxide environment resulted in an increase in moisture content. This is most likely attributed to some error in reporting the value. Ultimate analysis shows that there was no significant difference between the results of torrefaction using Nitrogen, Argon, and Carbon-dioxide. Further examination of the heat value analysis shows perhaps the most interesting results with torrefaction in a Carbon-dioxide environment resulting in a smaller increase in HHV when compared to the results from torrefaction using Nitrogen and Argon. The smaller HHV's when Carbon-dioxide was used as a purge gas are a result of the increased mass loss during torrefaction. For further reference the fuel properties of torrefied biomass on a dry and dry ash free basis are presented in Appendix B.

Table 4.5 – Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Nitrogen as the purge gas (reported on an as received basis unless otherwise noted).

	Mesquite	Juniper	Sorghum
Moisture	4.84	5.69	4.78
Volatile Matter	69.51	74.60	57.72
Fixed Carbon	23.26	18.63	25.38
Ash	2.39	1.08	12.12
Carbon	53.41	53.55	48.81
Oxygen	33.17	34.06	28.01
Hydrogen	5.33	5.42	4.97
Nitrogen	0.81	0.19	1.19
Sulfur	0.05	0.01	0.12
HHV _{TB} (kJ/kg)	19822	20099	19510
HHV _{RB} (kJ/kg)	16666	18987	15928
HHV _{TB,DAF} (kJ/kg)	21367	21558	23478
HHV _{DAF,RB} (kJ/kg)	20128	20584	19389
Empirical Formula (TB)	$C_{4.45}O_{2.07}H_{5.33}N_{0.057}S_{0.002}$	$C_{4.46}O_{2.13}H_{5.42}N_{0.014}S_{0.0003}$	$C_{4.07}O_{1.75}H_{4.97}N_{0.085}S_{0.003}$
Empirical Formula (RB)	$C_{3.63}O_{2.09}H_{4.98}N_{0.04}S_{0.001}$	$C_{4.11}O_{2.31}H_{5.68}N_{0.02}S_{0.0003}$	$C_{3.82}O_{1.88}H_{5.01}N_{0.08}S_{0.003}$

Table 4.6 – Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Argon as the purge gas (reported on an as received basis unless otherwise noted).

	Mesquite	Juniper	Sorghum
Moisture	3.56	4.14	5.02
Volatile Matter	70.45	74.52	60.55
Fixed Carbon	23.56	20.19	22.76
Ash	2.43	1.15	11.67
Carbon	54.07	54.88	47.87
Oxygen	33.68	34.00	29.12
Hydrogen	5.38	5.62	5.00
Nitrogen	0.84	0.20	1.22
Sulfur	0.04	0.01	0.10
HHV _{TB} (kJ/kg)	19819	20095	19507
HHV _{RB} (kJ/kg)	16666	18987	15928
HHV _{TB,DAF} (kJ/kg)	21081	21218	23415
HHV _{DAF,RB} (kJ/kg)	20128	20584	19389
Empirical Formula (TB)	C _{4.51} O _{2.11} H _{5.38} N _{0.06} S _{0.001}	C _{4.57} O _{2.13} H _{5.62} N _{0.014} S _{0.0003}	C _{3.99} O _{1.82} H _{5.00} N _{0.09} S _{0.003}
Empirical Formula (RB)	C _{3.63} O _{2.09} H _{4.98} N _{0.04} S _{0.001}	C _{4.11} O _{2.31} H _{5.68} N _{0.02} S _{0.0003}	C _{3.82} O _{1.88} H _{5.01} N _{0.08} S _{0.003}

Table 4.7 - Proximate, ultimate, and heat value analysis of the torrefied biomass (TB) with Carbon-dioxide as the purge gas (reported on an as received basis unless otherwise noted).

	Mesquite	Juniper	Sorghum
Moisture	4.3	6.25	4.3
Volatile Matter	71.14	73.19	62.83
Fixed Carbon	22.22	19.43	21.68
Ash	2.34	1.13	11.19
Carbon	53.25	53.24	48.03
Oxygen	33.93	33.78	30.12
Hydrogen	5.37	5.41	5.14
Nitrogen	0.77	0.17	1.12
Sulfur	0.04	0.02	0.10
HHV _{TB} (kJ/kg)	19464	19845	17780
HHV _{RB} (kJ/kg)	16666	18987	15928
HHV _{TB,DAF} (kJ/kg)	20848	21427	21039
HHV _{DAF,RB} (kJ/kg)	20128	20584	19389
Empirical Formula (TB)	C _{4.44} O _{2.12} H _{5.37} N _{0.06} S _{0.001}	C _{4.44} O _{2.11} H _{5.41} N _{0.012} S _{0.0006}	C _{4.00} O _{1.88} H _{5.14} N _{0.08} S _{0.003}
Empirical Formula (RB)	C _{3.63} O _{2.09} H _{4.98} N _{0.04} S _{0.001}	C _{4.11} O _{2.31} H _{5.68} N _{0.02} S _{0.0003}	C _{3.82} O _{1.88} H _{5.01} N _{0.08} S _{0.003}

With coal being the most widely used fossil fuel a comparison of the fuel properties of torrefied biomass to coal (Table 4.2) can provide good insight into the overall usefulness of torrefied biomass as a fuel. The fixed carbon content of mesquite and juniper torrefied in Nitrogen and Argon is only slightly less than that of Texas lignite. As fixed carbon content is the most important fuel property when evaluating solid fuels, the importance of the FC content of the torrefied biomass and lignite being relatively the same cannot be understated. Previous research [5] has shown that coal-biomass blends with a ratio of coal to biomass greater than 80:20 results in several combustion issues due to the fuel properties of the raw biomass. With the fuel properties of torrefied biomass being much better than raw biomass it is entirely feasible that blended fuels with a ratio of coal to torrefied fuel greater than 80:20 could be used in co-firing applications.

Knowing the actual HHV of the torrefied biomass (HHV_{TB}) the amount actual amount of energy retained can be calculated (see section 4.6.) Due to inherent mass loss form torrefaction the retained provides the percentage of the raw biomass retained within the torrefied biomass. The resulting calculated values of energy retained for all three biomasses in each purge gas environment can be seen in Table 4.8.

Table 4.8 – Calculated values of percent energy retained for torrefied biomass.

Biomass	Purge Gas		
	Nitrogen	Argon	Carbon-dioxide
Mesquite	88.74	87.73	84.47
Juniper	83.68	83.16	78.86
Sorghum	91.81	90.15	82.25

The energy retention calculations show that torrefaction in a Nitrogen environment resulted in the highest amount of energy being retained. Torrefaction using Argon as the purge gas had a slightly lower amount of energy retention when compared to Nitrogen. This coincides with the trends seen throughout experimentation, torrefaction using Nitrogen and Argon produce relatively the same results with almost minimal difference between the two purge gases. However, the energy retention of torrefaction in a Carbon-dioxide environment show that using Carbon-dioxide as a purge gas results in the lowest energy retention for all three biomasses

tested. The lower amount of energy being retained after torrefaction using CO₂ is a result of more volatiles being liberated via the Boudouard reaction (see section 4.5). Overall the results of large batch torrefaction of all three biomass using Nitrogen, Argon, and Carbon-dioxide as purge gasses are promising, with the exception of sorghum torrefied in a Carbon-dioxide environment the HHV's of the torrefied biomass are relatively the same.

Reviewing all of the analysis done the several suggestions can be made. From the TGA and DTG analysis (as well as other literature) it can be determined that a mild torrefaction temperature (240-260°C) will produce the best results. The research conducted in this thesis suggests that Carbon-dioxide could be used for as a torrefaction medium, however, the resulting biomass would be less desirable than a biomass torrefied using Nitrogen or Argon as the purge gas.

4.8 Grindability Analysis

Biomass samples that were torrefied in the laboratory oven also subjected to grinding and size distribution analysis to determine the effect of torrefaction on the grindability of the biomass. These studies were carried out as outlined in section 3.2.4 of this thesis. The results of initial size distribution analysis (Table 4.9) show that torrefaction of the biomass resulted in smaller particle sizes. These smaller particle sizes are a result of mass lost during the torrefaction process. Furthermore, it can be seen that there is a large weight percent of the un-ground Mesquite and Juniper does not pass through an 840 µm mesh. Since the Sorghum was received with a smaller particle size distribution there is only a drop in the weight percent of particles after the 149µm mesh size, which about 20% of the particles pass through.

After an initial size distribution was determined, the samples were ground for a set period of time (20 minutes) in order to keep the amount of energy consumed by grinding constant. After grinding the samples were again analyzed for size distribution. The size distributions of the ground samples can be seen in Table 4.10.

Comparing the ground sample size distributions to the un-ground size distributions it is clear that torrefaction increases the grindability of the biomass. While grinding had a minimal effect on the raw biomass (~5-10% increase in weight percent passing through 840µm mesh), grinding of the torrefied biomasses resulted in significantly more particles being of smaller size.

Both the torrefied Mesquite and Juniper samples saw an increase of roughly 20% more of the mass passing through an 840 μ m mesh size. For Sorghum the mass of torrefied biomass that passed through a 149 μ m mesh more than doubled.

For both Mesquite and Juniper, torrefaction using CO₂ resulted in a higher fraction of the ground biomass passing through an 840 μ m mesh size. However, the Sorghum samples torrefied in Nitrogen and Carbon-dioxide had roughly the same amount of mass pass through a 149 μ m mesh. This indicates that torrefaction using CO₂ may actually improve the grindability of the biomass more than torrefaction using Nitrogen.

Given that Sorghum was initially received in smaller particles than both Mesquite and Juniper and 100% of the mass of Sorghum passed through the first two sieves, if a different (smaller) set of sieves were used perhaps the same increase in grindability of Sorghum when using CO₂ would become apparent.

Overall torrefaction of the biomass, regardless of the environment, significantly improved grindability. Torrefaction using Carbon-dioxide further improved grindability when compared to Nitrogen. This is most likely a result of the higher mass loss observed during the torrefaction of biomass in a CO₂ environment.

Table 4.9 – Size distribution analysis for un-ground virgin and torrefied biomass.

Mesquite - Un-Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 840 μm
Raw	78.09	8.75	10.83	0.38	0.26	0.08	0.21	0.31	1.24
Torrefied - N ₂	71.07	9.57	16.15	0.93	0.64	0.34	0.36	0.38	2.64
Torrefied - CO ₂	77.42	7.92	12.25	0.63	0.74	0.28	0.20	0.24	2.09
Juniper - Un-Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 840 μm
Raw	44.95	17.12	34.31	2.14	0.75	0.07	0.15	0.31	3.42
Torrefied - N ₂	36.24	14.51	44.55	2.83	1.41	0.06	0.13	0.07	4.50
Torrefied - CO ₂	36.19	17.04	39.50	3.76	1.76	0.29	0.22	0.30	6.33
Sorghum - Un-Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 149 μm
Raw	0.00	0.00	12.39	14.43	52.41	10.15	4.28	5.60	20.03
Torrefied - N ₂	0.00	0.00	10.13	12.37	49.75	9.86	13.48	3.79	27.13
Torrefied - CO ₂	0.00	0.00	11.74	14.85	55.53	10.78	3.47	2.95	17.20

Table 4.10 - Size distribution analysis for ground virgin and torrefied biomass.

Mesquite - Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 840 μm
Raw	60.00	10.08	20.23	1.84	2.44	1.28	1.46	2.41	9.44
Torrefied - N ₂	42.15	8.40	25.40	3.72	8.95	3.10	1.82	4.56	22.15
Torrefied - CO ₂	31.20	7.35	18.67	22.16	6.02	5.49	2.65	3.92	40.24
Juniper - Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 840 μm
Raw	27.89	10.96	47.04	5.76	4.71	0.91	1.45	0.77	13.59
Torrefied - N ₂	15.99	7.75	47.56	8.56	8.99	2.64	1.66	6.61	28.46
Torrefied - CO ₂	14.90	7.16	44.01	7.95	9.20	4.78	4.42	6.41	32.76
Sorghum - Ground									
Sample	>2380 μm	2380 - 2000 μm	2000 - 840 μm	840 - 590 μm	590 - 149 μm	149 - 74 μm	74 - 53 μm	< 53 μm	%< 149 μm
Raw	0.00	0.00	8.97	11.78	50.95	12.78	5.35	8.44	26.57
Torrefied - N ₂	0.00	0.00	4.22	5.14	29.82	18.06	10.34	31.67	60.07
Torrefied - CO ₂	0.00	0.00	4.07	6.20	30.33	18.67	11.98	27.81	58.46

4.9 Hydrophobicity

Further tests were conducted on the raw and torrefied biomass to determine the effect that torrefaction has upon the naturally hydroscopic behavior of raw biomass. In order to test this the raw and torrefied biomass were submerged in water for 15 hours and weighed to determine the increase in weight due to moisture absorption. The “soaked” biomass also was subjected to moisture testing to determine the moisture content of the biomass after being submerged for 15 hours. The results of the hydrophobicity tests can be seen in Table 4.11.

Soaking the raw biomass for 15 hours resulted in a significant amount of weight being absorbed where as soaking the raw biomass resulted in a smaller increase in weight gain, specifically for Sorghum which saw a significant decrease in the amount of weight gained due to moisture absorption. Moisture tests on the biomass showed that the moisture content of the raw biomass increased significantly (see Table 4.1), with the moisture content of Juniper increasing the most (~11 times its initial moisture content.) The fact that the moisture content of Juniper increased the most is likely due to the raw Juniper having the lowest initial moisture content among the three biomass tested.

Moisture tests on the torrefied biomass soaked for 15 hour indicated much smaller increases in moisture content. Biomass torrefied in Nitrogen had a lower moisture content after soaking than biomass torrefied in Carbon-dioxide. This indicates that biomass torrefied in a Carbon-dioxide environment may degrade faster than biomass torrefied in Nitrogen when stored for long periods of time.

Table 4.11 – Results of hydrophobicity tests conducted on raw and torrefied biomass.

Raw Biomass					
Biomass	Initial Weight (g)	Soaked Weight (g)	Weight Gained (g)	% Weight Increase Due to Absorption	% Moisture in Biomass
Mesquite	24.991	57.389	32.398	230	58.29
Juniper	25.023	68.607	43.584	274	65.17
Sorghum	25.997	158.266	132.269	609	76.57
Torrefied Biomass - Nitrogen					
Biomass	Initial Weight (g)	Soaked Weight (g)	Weight Gained (g)	% Weight Increase Due to Absorption	% Moisture in Biomass
Mesquite	22.573	47.358	24.785	210	9.58
Juniper	21.963	48.517	26.554	221	11.49
Sorghum	18.119	84.778	66.659	468	14.31
Torrefied Biomass - Carbon-dioxide					
Biomass	Initial Weight (g)	Soaked Weight (g)	Weight Gained (g)	% Weight Increase Due to Absorption	% Moisture in Biomass
Mesquite	25.662	57.368	31.706	224	12.36
Juniper	21.14	51.887	30.747	245	12.52
Sorghum	15.563	72.637	57.074	467	25.58

5. CONCLUSIONS AND FUTURE STUDIES

Several conclusions can be drawn from the TGA/DTG analysis and fuel property analysis of the torrefied biomass. The use of Nitrogen and Argon as a purge gas during the torrefaction of the three biomass tested produced the same results. Torrefaction of all three biomass using Carbon-dioxide as the purge gas resulted in a higher weight loss. The higher amount of weight loss when using CO₂ can be attributed to the reaction of the CO₂ purge gas with fixed carbon contained within the biomass. Torrefaction of Mesquite and Juniper using CO₂ as the purge gas resulted in a visible shift in the peak lignin breakdown to higher temperatures. Furthermore, increasing the torrefaction temperature resulted in a decrease in the hemicellulose and cellulose peaks due to liberation of more light weight volatiles during torrefaction at higher temperatures.

Overall, Nitrogen, Argon, and Carbon-Dioxide are viable options as purge gases for torrefaction. The fuel analysis results of torrefaction of the three biomasses tested are in agreement with previous studies, in that:

- 1) Torrefaction of biomass results in a fuel with a larger HHV
- 2) The O/C ratio is decreased as a result of torrefying raw biomass

Furthermore, comparison of the torrefied fuels to low rank coal shows that the torrefaction of raw biomass can produce a fuel that is comparable to TXL coal in terms of fixed carbon content on an as received basis.

The results from torrefaction of the three biomass show that mesquite and juniper wood thermally degrade in relatively the same manner. Subtle differences in the DTG distributions of Mesquite and Juniper can be attributed to differences in chemical makeup between the two biomasses. Trends observed from the torrefaction of Mesquite and Juniper are much less apparent when applied to Sorghum, specifically increased weight loss when using CO₂ as the torrefaction medium which is attribute to the higher ash content of Sorghum. The thermal degradation profile of Sorghum appears to vary significantly from Mesquite and Juniper. As Mesquite and Juniper are woods and Sorghum is a grass, any further work with Sorghum should first proceed with the torrefaction of another species of grass and comparing the results to Sorghum in order to discern any common trends.

Overall, the use of Carbon-dioxide as a torrefaction medium results in a biomass with a smaller HHV than the same biomass torrefied in Nitrogen or Argon. Therefore, given the higher amount of weight loss with CO₂ and the smaller HHV the amount of energy retained in the torrefied biomass is lowest when torrefying in a CO₂ environment. However, grindability studies show that biomass that is torrefied in a CO₂ environment is easier to grind than biomass torrefied in N₂. That is biomass torrefied in a CO₂ environment will require less energy to pulverize. Hydrophobicity tests indicated that biomass torrefied in Nitrogen was slightly more resistant to moisture absorption than biomass torrefied in Carbon-dioxide. Furthermore, preliminary torrefaction tests using a TGA showed that reducing residence time will reduce the amount of mass loss when using CO₂ as a torrefaction medium. This appears to suggest that the amount of energy retained in biomass torrefied with CO₂ could be further controlled by varying residence time. It is entirely possible that the use of CO₂ as a torrefaction medium would require a shorter residence time to produce the same quality fuel as a biomass torrefied in a N₂ environment.

Considering all of these factors, it is suggested that Carbon-dioxide is a better torrefaction medium than Nitrogen and Argon. Although, higher weight losses and more moisture absorption were observed when using CO₂, the increased grindability and possibility that less energy would be required to produce high quality fuel make CO₂ the better torrefaction medium. Furthermore, given that biomass is considered CO₂ neutral, a process where the CO₂ emissions from the combustion or gasification of biomass could be used to torrefy raw biomass is an attractive prospect.

Future work should further investigate the effect of using CO₂ as a purge gas on biomass other than the ones tested in this thesis. Further investigation should be done into the weight loss trends when using CO₂ to obtain a concrete solution as to why CO₂ causes a higher weight loss during torrefaction. Further investigation of varying residence times when torrefying with CO₂ could provide more valuable insight into the weight loss characteristics of CO₂ torrefaction. This could also provide a way of optimizing several factors including energy retention and grindability when using CO₂ as a torrefaction medium.

6. REFERENCES

- [1] U.S. Energy Information Administration, International Energy Outlook 2010
<<http://www.eia.gov/oiaf/ieo/pdf/0484%282010%29.pdf>>, Accessed August 2011
- [2] U.S. Department of Energy, Carbon Sequestration Regional Partnerships
<<http://fossil.energy.gov/programs/sequestration/partnerships/index.html>> , Accessed August 2011
- [3] Arias B., Pevida C., Feroso J., Plaza M.G., Rubiera F., Pis J.J. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing Technology* 2007; 89(2): 169-175
- [4] Electric Power Monthly (2011): 1. U.S. Energy Information Administration. 20 July 2011.
<<http://www.eia.gov/cneaf/electricity/epm/epm.pdf>>, August 2011.
- [5] Thanapal S. S., Gasification of low ash partially composted dairy biomass with enriched air mixture. 2010 M.S. Thesis. Texas A&M University
- [6] Lawrence B. , Annamalai K., Sweeten J.M., and Heflin K. Cofiring coal and dairy biomass in a 29 KW furnace. *Applied Energy* 2009; 86(11): 2359-2372.
- [7] Annamalai, K and Puri, I. K., *Combustion science and engineering*, Boca Raton, Florida: CRC Press: Taylor and Francis; 2006.
- [8] Chen W.H, Kuo P.C., A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy* 2010; 35(6): 2580-2586
- [9] Prins M.J., Krysztof J. P. , Janssen F.J.J.G. More efficient gasification via torrefaction. *Energy* 2006; 31(15): 3458-3470
- [10] Chen WH., Hsu HC., Lu KM., Lee WJ., Lin TC. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. *Energy* 2011; 36(5): 3012-3021

- [11] Phanphanich M., Sudhagar M. Impact of Torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology* 2011; 102(2): 1246-1253.
- [12] Bridgeman T.G., Jones J.M., Williams A., Waldron D.J. An investigation of the grindability of two torrefied energy crops. *Fuel* 2010; 89(12): 3911-3918
- [13] Bridgeman T.G., Jones J.M., Shield I., Williams P.T., Torrefaction of reed canary grass, wheat straw, and willow to enhance solid fuel qualities and combustion properties. *Fuel* 2006; 87(6): 844-856
- [14] Prins M.J., Krysztof J. P., Janssen F.J.J.G. Torrefaction of wood Part 2. Analysis of products. *Energy* 2006; 77(1): 35-40
- [15] Prins M.J., Krysztof J. P., Janssen F.J.J.G. Torrefaction of wood Part 1. Weight loss kinetics. *Energy* 2006; 77(1): 28-34
- [16] Chen W.H., Kuo P.C. Torrefaction and co-torrefaction of hemicellulose, cellulose and lignin as well as torrefaction of the some basic constituents in biomass. *Energy* 2010; 36(2): 803-811
- [17] Raveendran K., Ganesh A., Khilar K.C., Pyrolysis characteristics of biomass and biomass components *Fuel* 2006; 75(8): 987-998
- [18] Demirbaş A. Estimating of structural composition of wood and non-wood biomass samples. *Energy Sources* 2005; 27(8):261-767
- [19] ASTM Standard d1103-60, 1977, Method of test for alpha cellulose in wood, ASTM International, Philadelphia, PA, 1977
- [20] Wu YM., Zhao ZL., Li HB., Fang HE. Low temperature pyrolysis characteristics of major components of biomass, *J. of Fuel Chem. and Tech.* 2009; 37(4): 427-432
- [21] Yang H., Yan R., Chen H., Lee D.H., Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007; 86(12-13): 1781-1788
- [22] Pimchuai A., Dutta A., Basu P. Torrefaction of agriculture residue to enhance combustible properties. *Energy & Fuels* 2010; 24(9): 4638-4645

[23] Martin B. Pyrolysis and ignition behavior of coal, cattle biomass, and coal/cattle biomass blends. 2006 M.S. Thesis. Texas A&M University

[24] BioEnergy Lists: Gasifiers & Gasification, Boudouard Equilibrium
<<http://gasifiers.bioenergylists.org/node/223>>, Accessed August 2011

APPENDIX A: PRINCIPLES OF TGA OPERATION

The TA Q600 TGA/DSC instrument is a highly accurate machine capable running a wide range of tests. For the studies done in this thesis the obtained measurements that were utilized were time, temperature, and weight. The Q600 utilizes two horizontal beams to measure sample temperature and sample weight. One beam being the reference beam is loaded with a reference pan, which act as a zero weight for calibration. The second beam is loaded with a test pan, initially left empty while the TGA undergoes a tare operation. During experimentation the test pan is loaded with a predetermined amount of sample.

The principle of the Q600 operation is relatively simple. Each beam is counterbalanced by metal weights (Fig. A.0.1), when a sample is loaded a magnetic counter force is applied to the sample beam to prevent deflection. As the sample weight increases or decreases the magnitude of the magnetic force adjusts accordingly to maintain zero deflection.

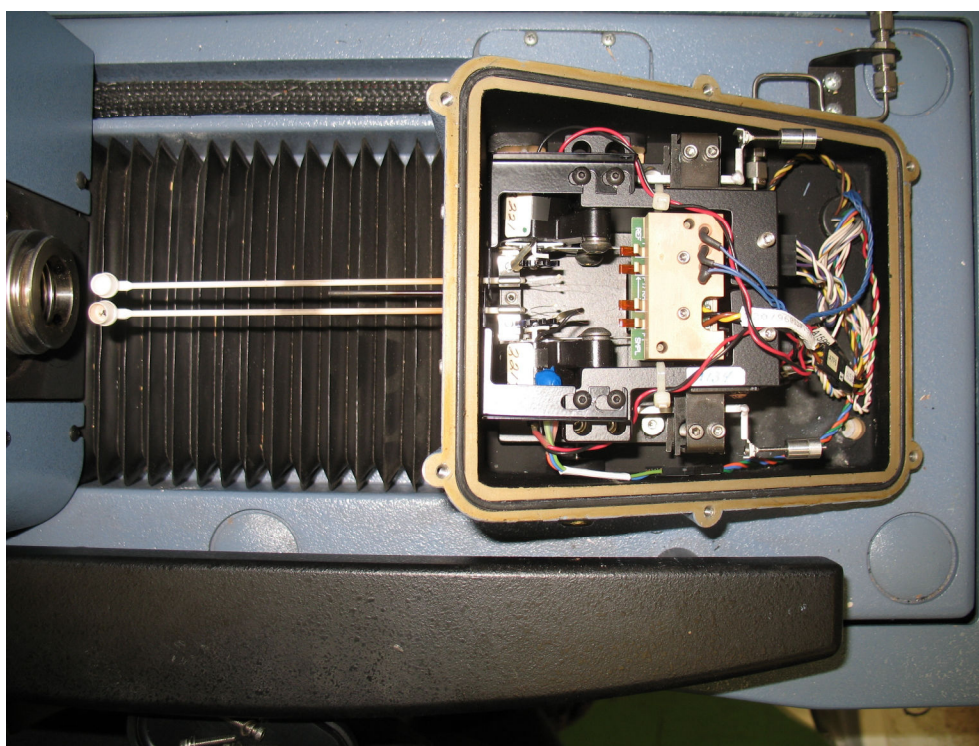


Fig. A.0.1 – TA Q600 beam and counter weight setup.

Consistent with electromagnetic theory the voltage required to generate the force is proportional to said force, the voltage is measured and through calibration the force required to keep the beam balanced can be measured. In solid fuel TGA analysis causes the sample to thermally degrade resulting in mass loss. As the mass of the sample decreases the voltage required to maintain zero deflection is measured and in turn the sample weight can be determined.

The Q600 is capable of providing data for several other tests including differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The exit port of the furnace can also be connected to an FTIR, usually via a heated transfer line, to measure the gasses produced during thermal degradation.

This information was obtained from Mr. Sean Kohl of TA instruments and Ben Lawrence Phd. Both have significant first hand experience working with the Q600 TGA/DSC.

APPENDIX B: RAW AND TORREFIED BIOMASS FUEL PROPERTIES

For further reference the fuel properties obtained via proximate, ultimate, and heat value analyses are presented on a dry and dry ash free basis.

Table B.1 – Raw biomass fuel properties on a dry basis

	Raw Biomass Dry Basis		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	78.24	82.84	71.20
Fixed Carbon	19.78	15.14	18.32
Ash	1.98	2.03	10.48
Carbon	51.62	52.33	49.89
Oxygen	39.74	39.30	32.88
Hydrogen	5.90	6.03	5.46
Nitrogen	0.73	0.30	1.18
Sulfur	0.04	0.01	0.12
HHV (kJ/kg)	19730	20167	17356
Empirical Formula *	$\text{CO}_{0.58}\text{H}_{1.37}\text{N}_{0.012}\text{S}_{0.0003}$	$\text{CO}_{0.56}\text{H}_{1.38}\text{N}_{0.005}\text{S}_{0.0001}$	$\text{CO}_{0.49}\text{H}_{1.31}\text{N}_{0.02}\text{S}_{0.0009}$
* - Formula Carbon normalized			

Table B.2 –Fuel properties of biomass torrefied in a Nitrogen environment presented on a dry basis.

	Nitrogen Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	73.05	79.10	60.62
Fixed Carbon	24.44	19.75	26.65
Ash	2.51	1.15	12.73
Carbon	56.13	56.78	51.26
Oxygen	34.86	36.11	29.42
Hydrogen	5.60	5.75	5.22
Nitrogen	0.85	0.20	1.25
Sulfur	0.05	0.01	0.13
HHV (kJ/kg)	20830	21312	20490
Empirical Formula *	$\text{CO}_{0.47}\text{H}_{1.2}\text{N}_{0.013}\text{S}_{0.0004}$	$\text{CO}_{0.48}\text{H}_{1.22}\text{N}_{0.003}\text{S}_{0.00007}$	$\text{CO}_{0.43}\text{H}_{1.22}\text{N}_{0.021}\text{S}_{0.0009}$
* - Formula Carbon normalized			

Table B.3 – Fuel properties of biomass torrefied in a Argon environment presented on a dry basis.

	Argon Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	73.05	77.74	63.75
Fixed Carbon	24.43	21.06	23.96
Ash	2.52	1.20	12.29
Carbon	56.07	57.25	50.40
Oxygen	34.92	35.47	30.66
Hydrogen	5.58	5.86	5.26
Nitrogen	0.87	0.21	1.28
Sulfur	0.04	0.01	0.11
HHV (kJ/kg)	20550	20963	20538
Empirical Formula *	$\text{CO}_{0.47}\text{H}_{1.19}\text{N}_{0.013}\text{S}_{0.0003}$	$\text{CO}_{0.47}\text{H}_{1.23}\text{N}_{0.003}\text{S}_{0.00006}$	$\text{CO}_{0.46}\text{H}_{1.25}\text{N}_{0.022}\text{S}_{0.0008}$
* - Formula Carbon normalized			

Table B.4 – Fuel properties of biomass torrefied in a Carbon-dioxide environment presented on a dry basis.

	Carbon-dioxide Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	74.34	78.07	65.65
Fixed Carbon	23.22	20.73	22.65
Ash	2.45	1.21	11.69
Carbon	55.64	56.79	50.19
Oxygen	35.45	36.03	31.47
Hydrogen	5.61	5.77	5.37
Nitrogen	0.80	0.18	1.17
Sulfur	0.04	0.02	0.10
HHV (kJ/kg)	20339	21168	18579
Empirical Formula *	$\text{CO}_{0.48}\text{H}_{1.21}\text{N}_{0.012}\text{S}_{0.0003}$	$\text{CO}_{0.48}\text{H}_{1.22}\text{N}_{0.003}\text{S}_{0.00002}$	$\text{CO}_{0.47}\text{H}_{1.28}\text{N}_{0.02}\text{S}_{0.0008}$
* - Formula Carbon normalized			

Table B.5 – Raw biomass fuel properties on a dry ash free basis.

	Raw Biomass Dry Ash Free Basis		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	79.82	84.55	79.54
Fixed Carbon	20.18	15.45	20.46
Ash	----	----	----
Carbon	52.66	53.42	55.73
Oxygen	40.54	40.11	36.73
Hydrogen	6.01	6.16	6.10
Nitrogen	0.75	0.30	1.31
Sulfur	0.04	0.01	0.13
HHV (kJ/kg)	20128	20584	19389
Empirical Formula *	$\text{CO}_{0.58}\text{H}_{1.37}\text{N}_{0.012}\text{S}_{0.0003}$	$\text{CO}_{0.56}\text{H}_{1.38}\text{N}_{0.005}\text{S}_{0.0001}$	$\text{CO}_{0.49}\text{H}_{1.31}\text{N}_{0.02}\text{S}_{0.0009}$
* - Formula Carbon normalized			

Table B.6 – Fuel properties of biomass torrefied in a Nitrogen environment presented on a dry ash free basis.

	Nitrogen Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	74.93	80.02	69.46
Fixed Carbon	25.07	19.98	30.54
Ash	----	----	----
Carbon	57.57	57.44	58.74
Oxygen	35.76	36.53	33.71
Hydrogen	5.75	5.81	5.98
Nitrogen	0.87	0.20	1.43
Sulfur	0.05	0.01	0.14
HHV (kJ/kg)	21367	21558	23478
Empirical Formula *	$\text{CO}_{0.47}\text{H}_{1.2}\text{N}_{0.013}\text{S}_{0.0004}$	$\text{CO}_{0.48}\text{H}_{1.22}\text{N}_{0.003}\text{S}_{0.00007}$	$\text{CO}_{0.43}\text{H}_{1.22}\text{N}_{0.021}\text{S}_{0.0009}$
* - Formula Carbon normalized			

Table B.7 – Fuel properties of biomass torrefied in an Argon environment presented on a dry ash free basis.

	Argon Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	74.93883629	78.68229332	72.6803505
Fixed Carbon	25.06116371	21.31770668	27.3196495
Ash	----	----	----
Carbon	57.52	57.95	57.46
Oxygen	35.83	35.90	34.95
Hydrogen	5.72	5.93	6.00
Nitrogen	0.89	0.21	1.46
Sulfur	0.04	0.01	0.12
HHV (kJ/kg)	21081	21218	23415
Empirical Formula *	$\text{CO}_{0.47}\text{H}_{1.19}\text{N}_{0.013}\text{S}_{0.0003}$	$\text{CO}_{0.47}\text{H}_{1.23}\text{N}_{0.003}\text{S}_{0.00006}$	$\text{CO}_{0.46}\text{H}_{1.25}\text{N}_{0.022}\text{S}_{0.0008}$
* - Formula Carbon normalized			

Table B.8– Fuel properties of biomass torrefied in a Carbon-dioxide environment presented on a dry ash free basis.

	Carbon-dioxide Environment		
	Mesquite	Juniper	Sorghum
Moisture	----	----	----
Volatile Matter	76.20	79.02	74.35
Fixed Carbon	23.80	20.98	25.65
Ash	----	----	----
Carbon	57.04	57.48	56.83
Oxygen	36.34	36.47	35.64
Hydrogen	5.75	5.84	6.08
Nitrogen	0.82	0.18	1.33
Sulfur	0.04	0.02	0.12
HHV (kJ/kg)	20848	21427	21039
Empirical Formula *	$\text{CO}_{0.48}\text{H}_{1.21}\text{N}_{0.012}\text{S}_{0.0003}$	$\text{CO}_{0.48}\text{H}_{1.22}\text{N}_{0.003}\text{S}_{0.00002}$	$\text{CO}_{0.47}\text{H}_{1.28}\text{N}_{0.02}\text{S}_{0.0008}$
* - Formula Carbon normalized			

APPENDIX C: PRELIMINARY CARBON-DIOXIDE RESIDENCE TIME STUDIES

For all previous experimentation the residence time was held constant in order to keep all of the tests consistent. From the results previously presented on the weight loss characteristics when Carbon-dioxide was used as a torrefaction medium it clear that CO₂ causes increased amounts of weight loss compared to biomass torrefied in Nitrogen or Argon. It was previously hypothesized that this is due to the reaction of Carbon-dioxide with the fixed carbon contained in the biomass (Boudouard reaction), and that the residence time of 1 hour allowed the reaction to significantly affect the amount of weight lost during torrefaction. With this in mind a preliminary study was conducted using shorter residence times when torrefying with CO₂.

Tests were conducted using the TGA in the same manner outlined previously (section 3.2.2). Two different residence times (15 minutes and 30 minutes) and residence temperatures (240°C and 280°C) were tested to investigate if shorter residence times would reduce the amount of mass lost during torrefaction with CO₂. Previous studies [3] have found that torrefaction in a Nitrogen environment with residence times between 30 minutes – 3 hours produced no significant changes in mass loss (and therefore no significant changes in energy retention.) A TGA thermo gram overlaying the six curves obtained is shown in Fig. C.0.1. Due to equipment failure the data for torrefaction at 280°C for a residence time of 30 minutes was not able to be obtained.

From the TGA thermogram it is clear that decreasing residence times when torrefying with Carbon-dioxide results in less mass lost during the torrefaction process. This appears to further indicate that residence time does in fact effect the impact the Boudouard reaction has upon the biomass, with shorter residence times allowing less time for the reaction to occur. This ultimately results in less fixed carbon being liberated. This hypothesis however cannot be confirmed as fuel property analysis would need to be completed on biomass torrefied at shorter residence times in a Carbon-dioxide environment. It is still possible although to estimate the amount of energy retained after the torrefaction process as done in section 4.6, the results these estimations are shown in Table C.1.

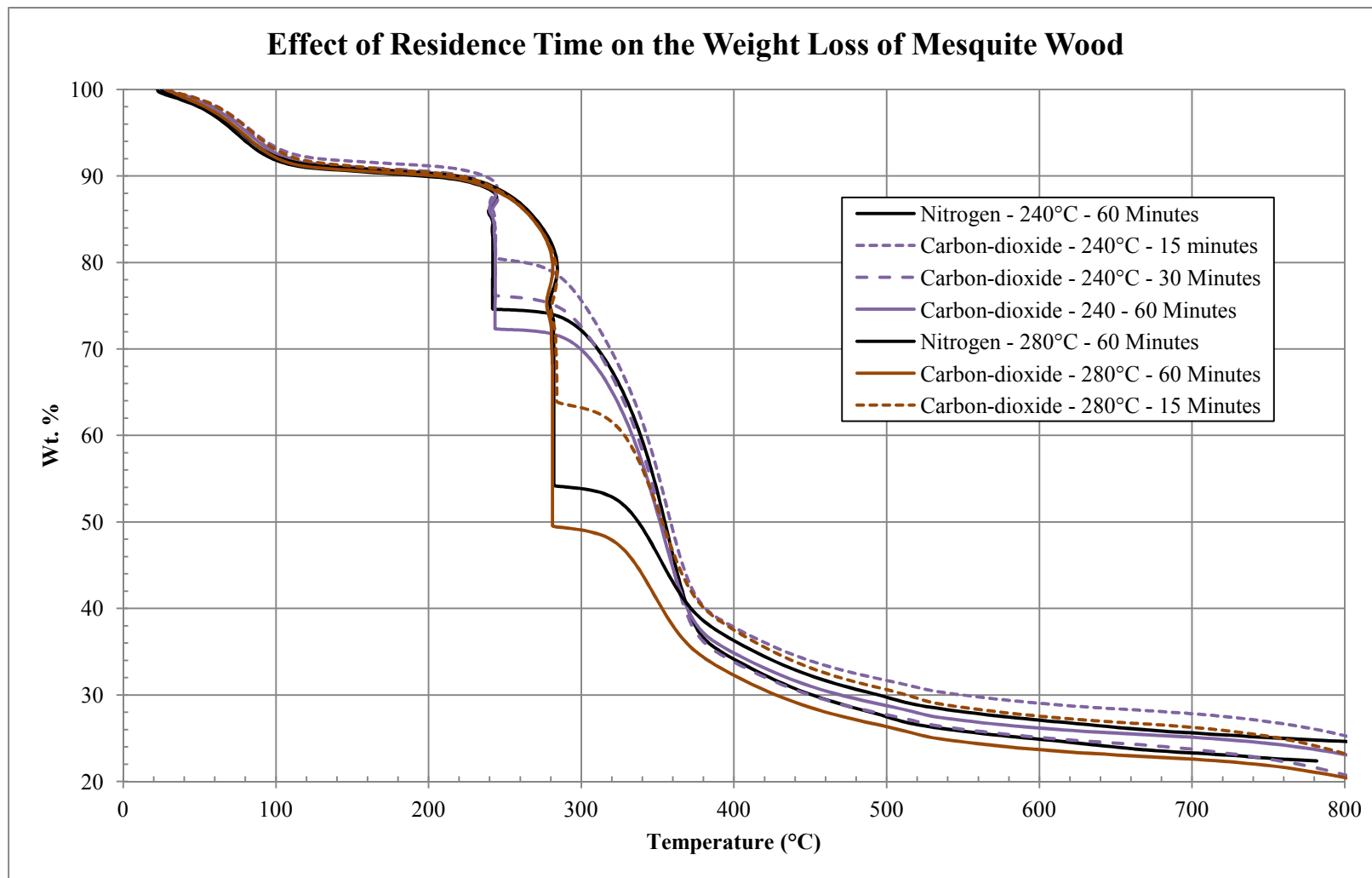


Fig. C.0.1 – The effect of residence time on the torrefaction of biomass in a Carbon-dioxide environment.

Table C.1 – Estimate energy retention for mesquite torrefied in a Carbon-dioxide environment at varying residence times.

	Residence Time (Minutes)		
Temp	15	30	60
240	90.66	87.45	84.66
280	78.47	----	65.70

VITA

Dustin E. Eseltine received his Bachelor of Science in mechanical engineering technology from Wentworth Institute of Technology in 2008, where he graduated cum laude. He entered the mechanical engineering program at Texas A&M University in August 2009. He received his Master of Science from Texas A&M University in 2011. His research interests include thermodynamics and combustion. He plans on pursuing a PhD in mechanical engineering at Texas A&M University under the advisement of Dr. Andrea Strzelec researching diesel engine particulates.

Mr. Eseltine may be reached at Mechanical Engineering 3123 TAMU College Station, TX 77843. His email is eseltined@gmail.com