CHARCOAL IN A NUTSHELL: BIOCARBON PRODUCTION FROM CELLULOSE, NORWEGIAN WOOD, MACADAMIA NUTSHELLS AND SEWAGE SLUDGE

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAI‘I AT MĀNOA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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Keywords: biocarbon, pressure, charcoal, waste, cellulose, pyrolysis, fixed carbon yield
It’s no trick to get the right answer when you have all the data. The real creative trick is to get the right answer when you have only half of the data in hand and half of it is wrong and you don’t know which half is wrong. When you get the right answer under these circumstances, you are doing something creative.

Melvin Calvin, Following the Trail of Light: A Scientific Odyssey
ACKNOWLEDGMENTS

I owe a tremendous debt of gratitude to you, Dr. Antal. In the first place for having unfolded me the hitherto uncharted charms of charcoal. It probably comes as a surprise to you that even (clean) charcoal allows for a rhyme and an alliteration or two.

Thanks for having given me the opportunity to study and to work at the University of Hawaii. I will treasure the help I received from you, not just in my professional but also in my personal life. I will be grateful for life, and be thinking of these four dazzling years of carbonization, and not only, I assure you, when I will be enjoying, somewhere in Norway or Belgium, a *gratin dauphinois* or *soupe à l'oignon gratinée*.

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ABSTRACT

While progressively diminishing our reliance on fossil fuels, it is of paramount importance to keep advancing low-carbon economic growth. A crucial role can be played by clean and efficient flash carbonization of biomass into biocarbon. This thesis reviews several elevated-pressure flash carbonization experiments, pyrolyzing varying biomass feedstocks and using different types of reactors. Renewed lab-scale sewage sludge carbonization experiments were intended to remedy shortcomings with respect to the experimental reproducibility and inaccurate analyses of heavy metal concentrations that have come to light in our previous work on sewage sludge carbonization. In support of the Norwegian ferrosilicon industry, local birch, spruce and GROT were carbonized in the lab-scale reactor, with a view to analyzing the impact of pressure, soft versus hard wood and FC canister insulation on their respective fixed carbon yields. Demo-scale reactor macadamia nutshell carbonization experiments (creating charcoal with fixed carbon contents of 97%) taught us how to avoid fumes from being emitted and to better monitor the self-designed thermal afterburner. Avicel cellulose carbonization experiments conducted under varying elevated pressures in the upgraded Wall-Heated Tubing Bomb Reactor produced, while showing evidence of a molten phase, high-quality solid pieces of charcoal. They enabled us to achieve 98% of the theoretical fC yield of cellulose.
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<td>Air to Biomass Ratio</td>
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</tr>
<tr>
<td>AC</td>
<td>4 cylinder Air-Cart</td>
<td>/</td>
</tr>
<tr>
<td>ACT</td>
<td>Atmospheric Condensates Trap</td>
<td>/</td>
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<tr>
<td>ADSG</td>
<td>Agricultural Diagnostic Service Center</td>
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<tr>
<td>APLR</td>
<td>Annual Pollutant Loading Rates</td>
<td>kg/ha/year</td>
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<tr>
<td>AR</td>
<td>As Received</td>
<td>/</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
<td>/</td>
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<tr>
<td>CAB</td>
<td>Catalytic After Burner</td>
<td>/</td>
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<tr>
<td>CB</td>
<td>Carbon (mass) Balance</td>
<td>/</td>
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<tr>
<td>CAPLR</td>
<td>Cumulative Pollutant Loading Rates</td>
<td>kg/ha</td>
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<tr>
<td>d.a.f.</td>
<td>dry ash-free</td>
<td>/</td>
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<tr>
<td>db</td>
<td>dry basis</td>
<td>wt%</td>
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<tr>
<td>DDV</td>
<td>Down Draft Valve</td>
<td>/</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
<td>/</td>
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<tr>
<td>EU</td>
<td>European Union</td>
<td>/</td>
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<tr>
<td>FAO</td>
<td>Food and Agriculture Organization</td>
<td>/</td>
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<tr>
<td>fC</td>
<td>Fixed Carbon</td>
<td>wt% dry basis</td>
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<tr>
<td>FC</td>
<td>Flash Carbonization</td>
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<tr>
<td>FRPV</td>
<td>Flow Regulating Propane Valve</td>
<td>/</td>
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<tr>
<td>GHG</td>
<td>Green House Gas</td>
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<tr>
<td>GROT</td>
<td>G&amp;ren Och Toppar</td>
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<tr>
<td>HEPA</td>
<td>High-efficiency particulate arrestance</td>
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<tr>
<td>HHT</td>
<td>Higher Heating Temperature</td>
<td>ºC</td>
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<tr>
<td>HHV</td>
<td>Higher Heating Value</td>
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<tr>
<td>IV</td>
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<tr>
<td>MAWP</td>
<td>Maximum Allowable Working Pressure</td>
<td>psi or MPa</td>
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<tr>
<td>MC</td>
<td>Moisture Content</td>
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<td>MMV</td>
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<tr>
<td>NPT</td>
<td>National Pipe Thread</td>
<td>/</td>
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<tr>
<td>NTNU</td>
<td>Norges teknisk-naturvitenskapelige universitet (Norwegian University of Science and Technology)</td>
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<tr>
<td>PAV</td>
<td>Pneumatically Activated Valve</td>
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<tr>
<td>PCT</td>
<td>Pressurized Condensates Trap</td>
<td>/</td>
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<tr>
<td>PDU</td>
<td>Process Development Unit</td>
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<tr>
<td>PT</td>
<td>Propane Tank</td>
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</tr>
<tr>
<td>PV</td>
<td>Propane Valve</td>
<td>/</td>
</tr>
<tr>
<td>R3-Laboratory</td>
<td>Renewable Resources Research Laboratory</td>
<td>/</td>
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<tr>
<td>SLRV</td>
<td>Spring-Loaded Relief Valve</td>
<td>/</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
<td>/</td>
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<tr>
<td>t</td>
<td>tonne, 1000 kg</td>
<td>/</td>
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<tr>
<td>TAB</td>
<td>Thermal Afte Aspired Air Burner</td>
<td>/</td>
</tr>
<tr>
<td>TGA</td>
<td>ThermoGravimetric Analysis</td>
<td>/</td>
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<tr>
<td>TC</td>
<td>Thermo Couple</td>
<td>/</td>
</tr>
<tr>
<td>VariAC</td>
<td>Variable Auto Transformer</td>
<td>/</td>
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<tr>
<td>VFA</td>
<td>Valve Forced Air</td>
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<tr>
<td>VM</td>
<td>Volatile Matter</td>
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<tr>
<td>VNAA</td>
<td>Valve Naturally</td>
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<tr>
<td>wb</td>
<td>wet basis</td>
<td>wt%</td>
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<tr>
<td>WHITB</td>
<td>Wall Heated Tubing Bomb</td>
<td>/</td>
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<tr>
<td>WHITBS</td>
<td>Wall Heated Tubing Bomb System</td>
<td>/</td>
</tr>
<tr>
<td>WWTP</td>
<td>Waste Water Treatment Plant</td>
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CHAPTER 1
INTRODUCTION

1.1 A long-awaited mindset change

On August 27, 1859, “Colonel” Drake hit oil in a small village named Titusville, PA. Drake had given himself the title Colonel as a way to prevent people from calling him a lunatic for drilling in the ground. Yet Drake was the starting point for an oil boom that would hit Philadelphia, the USA and the world. Eventually, every industry would be critically dependent upon oil, and countries would willingly wage war over what is now commonly referred to as ”black gold”. Eleven years later, John D. Rockefeller, the father of oil, formed the Standard Oil Company, which would dominate the oil industry and which became the first (and biggest) multinational company [7]. On June 2014, his descendants divested $50 billion from coal, tar sands and other fossil fuels [8]. There is a happy irony in that this family, a forerunner in fossil fuels, is now divesting from those same fuels, in the hope of slowing down the pace of global warming, thus becoming a big game-changer in the renewable energy domain. Although even now only 1% [8] of the Rockefeller family fortune is invested in renewable and alternative energies, this change shows an evolution in mindsets.

In June 2015, Norway’s $890 billion pension fund decided to pull out significant investments out of mining and power companies that generate more than 30 percent of their output or revenue from coal [9]. The investment banking firm Axa [10] and the Church of England [11] are following Norway’s example, pulling out $560 million and $1.2 billion, respectively, from the coal-powered sector. Universities such as Stanford and even our own alma mater, the University of Hawaii [12, 13], cities including Seattle and San Francisco, and several high net worth companies are now massively divesting from fossil fuels. This move clearly demonstrates how concerned companies, religious institutions, universities, pension funds, local authorities and associations are about their public image. Such mindset changes are needed to make renewable energy work and to radically redirect investment into clean energy solutions, including technologies to harness solar energy, wind power, geothermal energy and biomass fuels. Focus henceforth should be on investment targeting sustainability-oriented research and innovation aimed at keeping the planet’s remaining fossil fuels in the ground and on developing cleaner and more efficient energy sources or technologies.

At the same time, while investing in a greener and sustainable future in an attempt to avoid climate armageddon, there is a need to integrate environmental sustainability and economic growth. It is also glaringly crucial, within the limits of our planet, to keep supporting (low-carbon) economic growth, which is the basis for improvements in the standard of living. The time has come to shift emphasis from fossil fuel and greenhouse gas issues to innovation issues and to develop innovative
green solutions that can power economic growth, innovations that cost less, destroy less and benefit all. One such green solution is the highly-efficient leading-edge carbonization technology developed at the Hawaii Natural Energy Institute, i.e. the thermochemical conversion of biomass into biocarbon for a great many agricultural and industrial applications.

1.2 What’s next? Shifting focus from emissions to innovation

Disinvestment from fossil fuels is certainly an important step in the right direction: hallelujah! But what’s next? The greatest threat of a catastrophic rise in global temperatures comes from the world’s reliance on the fossil fuels responsible for greenhouse gas emissions. Global climate change and depletion of the oil supplies, which soon will no longer be able to meet global energy demand, will inevitably coax world economies to progressively abandon oil and fossil fuels as the primary energy source.

As generating energy from biomass and using clean and efficient carbonization technologies could significantly contribute to solving both problems, this could be a scenario worth considering and investing in. Under oxygen-deprived conditions, fast carbonization thermally transforms biomass into bio-oil, syngas and charcoal. The application of the charcoal by-product to soils may be the key to sustainability, as the carbon in the soil-applied charcoal is removed from the atmosphere and sequestered for thousands of years, a win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil fertility and water quality.

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Leaving the use of charcoal as an energy generator and its climate-smart benefits aside, it is also an industrial commodity that can conveniently replace fossil fuels in a myriad of uses and industrial applications, in both the metallurgy industry as a smelting fuel for iron ore and in the silicon chip industry as a reductant for the manufacture of pure silicon from quartz, to name but two. The exclusive use of residual waste as a feedstock during the Flash Carbonization (FC) process is significant, in that it makes less heavy demands on forest resources and avoids deforestation altogether. Moreover, converting agricultural residues, forestry waste and municipal biomass into high-quality charcoal is likely to bring down the greenhouse gas emissions that would otherwise have been released by the natural decomposition or burning of the waste.

1.3 Pyrolysis of biomass

Pyrolysis, derived from the ancient Greek pyro- (fire) and -lysis (decomposition into constituent parts), is a low-oxygen, high-temperature process that thermo-chemically decomposes biomass - materials that would otherwise go to waste - into a gaseous component, liquid bio-oil, and a solid residue containing the valuable fixed carbon (fC). Pyrolysis, which leaves predominantly carbon
as the residue, is called carbonization. Due to environmental considerations and the increasing demands of energy worldwide, biomass pyrolysis is given a great deal of attention these days, as it offers the opportunity to process agricultural residues, wood wastes and municipal solid waste into clean energy.

The syngas byproduct of biomass pyrolysis can be combusted for use in steam and electricity production [14], whereas the bio-oil is valuable because of the advantages it offers in storage, transport and versatility in applications where it replaces petrol, gasoline and diesel [15]. Not only does charcoal, when put into the soil, sequester carbon for centuries or even millennia, it can also considerably improve soil fertility, curtail deforestation and wood-burning for fuel. Biochar in that respect can be considered a blessed instrument in tackling climate change without crippling the economy. A unique combination of still other extremely useful properties makes biocarbons eminently suitable for many applications ranging from potting compost to the production of pure silicon used in the semiconductor industry [16].

Creating charcoal does hardly require really advanced technology. Slow pyrolysis is known to have been practised by the ancient Chinese. In fact, the benefits of biochar as a soil amendment were discovered thousands of years ago by Amazonian aborigines who mixed a combination of charcoal and organic matter in the soil and used the process to enhance crop production in the poor soils of the Amazonian rain forests of Brazil. Portuguese colonists called it terra preta, which is Portuguese for "black earth".

There are many ways to make biocarbons, but all of them involve the heating of biomass with little or no oxygen to prevent combustion. Early pyrolysis technology harvested neither bio-oil nor syngas and was characterized by slow production, low charcoal (and/or fixed carbon (fC)) yield and excessive air pollution.

Present-day pyrolysis systems enhance these traditional methods of creating charcoal by reducing pollution and by capturing and using the liquid and volatile by-products. During the last quarter of the previous century there was a trend towards minimizing charcoal yields. Because of the energy crisis that struck the world in that period, considerable efforts were directed towards developing fast pyrolysis processes maximizing the production of liquid fuels to the detriment of the gas and char byproducts [16].

By further increasing productivity and efficiency, Flash Carbonization and other high pressure carbonization processes in the $R^3$-Laboratory take pyrolysis one step further. They permit to obtain formidable biocarbon yields in an exceptionally short time-span, while recovering the pollutants
generated by the process. Throughput, efficiency and fixed carbon yields are maximized and reaction times are kept to a minimum, which in turn minimizes labor input and thus makes biomass carbonization economically viable.

1.4 Charcoal production across the globe

The Food and Agriculture Organization (FAO) of the United Nations provides wood charcoal data that are considered reliable, but as the FAO states, most of the data are a combination of official, semi-official, estimated and calculated numbers. In 2012, about 50 million metric tonnes (51,280,000 tonnes [2] versus 49,807,094 tonnes [17], note different figures from the same organization, depending on the method of data retrieval) of wood charcoal was produced worldwide compared to 7881 million metric tonnes of coal [18].

The top three wood charcoal producers in the world are Brazil, Nigeria and Ethiopia. The charcoal needs of Brazil tripled for use in its large steel industry (Brazil used to be the lowest cost steel producer in the world [19]), causing massive deforestation and CO$_2$ emissions [20]. The fact is that steel produced with unsustainable charcoal emits nine times more CO$_2$ per tonne of steel than coal. Nigeria, Ethiopia and Africa as a whole are the largest charcoal producers, as more than 10% of their populations use charcoal for cooking [21]. In countries such as Kenya, over 80% of the people rely on charcoal as a prime energy source.

Figure 1.1 illustrates which countries and regions contribute most to global charcoal production, and also shows that charcoal production in Europe and North America is insignificant. Charcoal production in Brazil decreased after 2008 because of the economic turn-down, but it seems to have been recovering in the following years.
In 2013, the global demand for coal kept increasing (coal remains the fastest growing fossil fuel), mainly due to the high demand in China [22]. The production of coal in the US dropped 3.1% falling below 1 billion short tons for the first time (984.8 million short tons). Coal consumption in the US increased by 4% to 924 million short tons (93% of which was used for electric power generation) [23].

Coal is still the number one fossil fuel used today, delivering over 30% of global primary energy demand. Forty percent is used for electricity generation, while over 70% of steel is made with coal. Fifteen percent of mined coal (1.2 billion short tons) is used in the steel industry [24]. Some countries produce and use more coal than others, for example China produces four times more coal than the US (totaling over 3,500 million short tons), while countries including South Africa depend on coal for 93% of their electricity needs. In Germany, for comparison, this figure is as low as 44%.

The use (and combustion) of these massive amounts of coal means that even larger amounts of \( CO_2 \) will be emitted into the atmosphere. The carbon in coal burns according to the following stoichiometric ratios:

\[
C + O_2 \rightarrow CO_2
\]  

(1.1)
Coal is not pure carbon, and Table 1.1 shows the different classes of coal and their mined amounts (the assumption is that all mined coal is also consumed in the US). Each of these classes of coal have a % of carbon [25]. For every kg of C or carbon burned, 44/12 kg of $CO_2$ is generated.

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>US Annual Production metric tonnes</th>
<th>Low Range</th>
<th></th>
<th>High Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon Content wt%</td>
<td>Carbon Mass million tonnes</td>
<td>CO$_2$ Produced million tonnes</td>
<td>Carbon Content wt%</td>
</tr>
<tr>
<td>Anthracite</td>
<td>1,948,182</td>
<td>93</td>
<td>1.81</td>
<td>6.64</td>
</tr>
<tr>
<td>Bituminous</td>
<td>428,348,182</td>
<td>80</td>
<td>342</td>
<td>1,260</td>
</tr>
<tr>
<td>Sub-Bituminous</td>
<td>394,806,364</td>
<td>75</td>
<td>296</td>
<td>1,090</td>
</tr>
<tr>
<td>Lignite</td>
<td>70,208,182</td>
<td>60</td>
<td>42.1</td>
<td>155</td>
</tr>
<tr>
<td>Total</td>
<td>2,512</td>
<td>Total</td>
<td>2,820</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1 shows that the US is responsible for 2,512-2,820 million metric tonnes of $CO_2$ emissions in 2014.

To put this into perspective: the US signed Kyoto’s protocol in Copenhagen (but did not ratify the treaty) to reduce net green house gas (GHG) emissions by 17% below 2005 levels by 2020. This translates into a reduction of 990 million metric tons of $CO_2$ emissions. We only need to reduce coal consumption in the US by 35-39% to achieve this goal.

If we want to stop coal consumption, we will have to look for clean alternatives and charcoal might be the choice.

Charcoal was initially the preferred raw material for activated carbon production. Because of environmental and economic constraints, coal was used as a replacement to manufacture activated carbon. Activated carbon is a popular means of purifying waste air (especially with the newly introduced mercury standards [26]) and water streams [27], but it can also be used as a digestive aid [28] or to mine precious metals such as gold [29].

During World War II, coconut charcoal-filled gasmasks were crucial to the US troops around Ypres in Belgium, but today the world’s largest producer of activated carbon is China with an output of 588,800 tons in 2014 (over 40% of the world’s production), 65% of which was activated charcoal [30]. In the US, the two main manufacturers of activated carbon are Calgon Carbon and
Cabot Norit, together responsible for an output of 135,000 tons of coal based activated carbon per year.

Charcoal used to be the preferred reducing agent for blacksmiths in the middle ages [31], but was gradually replaced by coal despite its superior characteristics (charcoal contains no sulfur and less ash). Because of these traits, Elkem, a leading European Ferrosilicon smelter, favors charcoal over coal, but is still carrying out research on making the use of Norwegian charcoal environmentally and financially possible [32]. In the chapter on Flash Carbonization of Norwegian wood, we go deeper into this subject.

Charcoal is not cheap, various papers report prices between 162 and 780 $/t [33] [16]. The coal price in the US in 2013 was between 10-60 $/t, depending on the grade of coal [34]. Charcoal would be too expensive and of too high a quality to be used as regular ‘steam’ coal or coal burned to generate electricity. Charcoal could replace the 18,506,000 metric tonnes of metallurgical coals (which cost up to $400/tonne, but recently the price has dropped to $93/tonne [35]) used yearly in the US and reduce emissions by over 68,000,000 metric tonnes. This is 7% of the Kyoto reduction for the US.

1.5 Objective of this thesis

This thesis extensively reviews several elevated-pressure flash carbonization experiments conducted at the Hawaii Natural Energy Institute (University of Hawaii), using different types of biomass feedstocks (sewage sludge, Norwegian wood, macadamia nutshells and avicel cellulose) and different types of reactors (Flash Carbonization Lab-Scale reactor, Flash Carbonization Demo-Scale reactor and Wall-Heated Tubing Bomb Carbonization reactor (WHTB)). Through the manipulation of pressure, moisture content and gas flow, we have been able to generate fixed-carbon yields that approach, and even attain, the thermochemical equilibrium limit in a small time-frame of some thirty minutes.

The first part of my thesis, partially elaborating on my Master of Science in Bioengineering master thesis 'Flash Carbonization of biomass' (University of Ghent - Belgium) henceforth referred to as the "Ghent master thesis", deals with the lab-scale flash carbonization of sewage sludge sourced from the Hawaii Kai waste water treatment plant. A description is given of the lab-scale reactor apparatus and experimental procedures used, but the main focus is on the concentration and distribution of heavy metals in the sewage sludge charcoal.

Shortcomings in the Ghent master thesis are pointed out with regard to the reproducibility of the flash carbonization experiments previously performed, inaccuracies in the analyses of heavy metal concentrations in the sludge charcoal samples, and the need for additional analyses to be carried
out in a broader selection of laboratories. Between 2011 and the present day, numerous additional experiments have been conducted at duplicate conditions. The additional heavy metal analyses from these have enabled us to better predict heavy metal behavior during flash carbonization. This four-year comparative look back has also allowed us to make a better assessment of the (economic) viability of the use of sewage sludge biochar globally and to better gauge the biochar properties needed for a successful implementation of biochar as a soil fertility amendment.

The second chapter reviews lab-scale flash carbonization experiments under elevated pressure using Norwegian wood as a feedstock. Norway’s silicon and ferrosilicon industry has been urged to reduce fossil CO₂ emissions by increasing the use of charcoal as a substitute for coal and coke in the reduction process. As charcoal is not produced in this country, large amounts of it are imported from Indonesia. Norway now intends to produce charcoal locally using optimum carbonization techniques from local biomass and forestry waste. That is where our pressurized flash carbonization experiments come in. Birch, spruce and GROT samples (GRenar Och Toppar, i.e. branches and tops), sent to us by the Norwegians, were dried and then carbonized, enabling us to analyze the impact of pressure, flow rate and FC canister insulation on their respective fixed carbon yield. Unique is the comparison that could be made between fixed carbon yields from soft wood (spruce) versus hard wood (birch).

The third chapter reviews the flash carbonization of macadamia nutshells in the Demo-Scale Flash Carbonization reactor. In some of the experiments, dark brownish fumes were released during the carbonization. To eliminate these emissions, we used a trial-and-error method to adequately monitor the performance of the self-designed thermal afterburner, and to thereby accurately determine the endpoint of the carbonization.

The fourth chapter discusses Avicel cellulose carbonization experiments performed in the upgraded Wall-Heated Tubing Bomb (WHTB) apparatus, under varying elevated pressures. The carbonization in the WHTB moves into a new world as the reactions occur under a constant volume regime in sealed vessels, while the pyrolysis experiments conducted in our lab scale and demo scale reactors (chapter 2.14) involved carbonization under constant pressure. This enabled us to realize the theoretical thermochemical equilibrium value of the fixed-carbon yield of cellulose. The WHTB is capable of producing, from packed cellulose feed, high quality solid pieces of charcoal, which remarkably show evidence of a molten phase. The analysis of the effect of sand bath temperature and tubing bomb pressure and the observation of a liquid phase during the charcoal formation affords a better insight in the kinetic behavior and reaction mechanisms of cellulose pyrolysis.
CHAPTER 2
FLASH CARBONIZATION

2.1 Introduction

Research directed by Professor Michael J. Antal, Jr. at Princeton in the 1980s, [5][4], which was continued in the R3-laboratory [36] [37] [38] [39] of the University of Hawaii, led to the introduction of a novel carbonization process for making biocoal or charcoal in an efficient and especially fast way. The patented invention [40]), designated 'Flash Carbonization', lived up to its name: any kind of biomass was carbonized 'in a flash'.

What distinguishes the FC apparatus from other, conventional carbonizers is the use of elevated pressure during operation. Generally, pyrolysis is carried out at atmospheric pressures (or even at vacuum to enhance liquid yields [41]), except for gasification, for which high pressures are common practice.

It was discovered that pressure, and the subsequent low flow rates thereby created, enhance both pyrolysis and combustion processes. These higher pressures (and low flow rates) cause the tarry vapors to be compressed and to be kept within the biomass for a longer time, resulting in more secondary decomposition. In addition to this, the rate of decomposition is increased, because of the higher partial pressure of the tarry vapors [6]. These tarry vapor reactions on the solid charcoal surface are also called ”secondary char reactions” and are exothermic. Primary char reactions are endothermic, but by increasing the pressure, the overall reaction can become exothermic, lessening the total amount of heat needed to fully carbonize the biomass bed.

Overall, when working at higher pressures and low flow rates, increased charcoal and fC yields have been observed, together with a more uniform charcoal bed; the high pressures promote heat transfer within the reactor as well [42]. The FC apparatus has been able to attain up to 80% of the calculated thermochemical equilibrium limit at elevated pressures of 1 MPa.

2.2 Lab-scale reactor

The Flash Carbonization Lab-Scale reactor became a real workhorse for the R3-Laboratory. Many papers were published using any feedstock imaginable, including leucaena [6] and oak wood, corncobs (the most abundant agricultural waste product in the US) [6] [43] [44], macadamia nutshells from the Big Island of Hawaii, wood sawdust, Christmas tree chips, Hungarian sunflower
shells [45], coconut, eucalyptus, bana grass [46], alder, birch, pine and spruce wood, rice hulls, sewage sludge [47] [48] and garlic processing waste [49].

2.2.1 Apparatus and experimental procedures

The description of the FC apparatus, together with the operating instructions below, is provided with adequate details to allow anyone with general engineering knowledge to reproduce the experiments done.

Overview

I began working on the FC apparatus in late 2011 and it quickly became my preferred 'go-to' pressurized vessel. Before any experiments were carried out, one of the many safety systems was evaluated. It cannot be emphasized enough that when working with pressurized vessels, safety systems should be installed and tested on a regular basis. It is easy to get an estimation of how much energy is stored in a pressure vessel by calculating the work needed to compress air, assuming isothermal conditions:

\[ W_{A\rightarrow B} = \int_{A}^{B} pdV = \int_{A}^{B} \frac{nRT}{V} dV = nRT \int_{A}^{B} \frac{1}{V} dV = nRT \ln \frac{V_{A}}{V_{B}} = nRT \ln \frac{P_{B}}{P_{A}} \]  

(2.1)

Since under isothermal conditions:

\[ P_{A}V_{A} = P_{B}V_{B} \]  

(2.2)

Assume we have an industrial "size 300" high pressure cylinder with an internal volume of 50 liters filled to 21 MPa of an ideal gas. The energy in this amount of compressed ideal gas is 5.6 MJ which is about 1.3 kg of TNT.

The text Steam boiler explosions [50] will give the reader an appreciation for pressure vessel safety. Written in 1903 it analyzes disastrous events in which metal pieces weighing over 2,300 kg were launched into the air, over 150 m. Note that during the pyrolysis of biomass, we are not dealing with the large amounts of water present in boilers. The outgassing and combustion of the biomass results in an extra rise in pressure.

The burst diaphragm of the FC lab reactor no longer displayed its release pressure clearly due to tarry deposits from previous experiments. It took several evenings to determine the exact burst pressure of this particular safety system: 2.77 MPa (387 psig). The next operator of the FC apparatus may save significant time by reading this short material section 2.2.1.
The burst diaphragm is now equipped with additional labels to avoid situations like this in the future, illustrating the importance of another research lab skill: the ability to label well.

**Apparatus**

The FC reactor is separate from the FC pressure vessel and the FC canister, which facilitates loading and unloading. The unit itself was built and certified as a power boiler in 1994, with a Maximum Allowable Working Pressure (MAWP) of 870 psig or 6.10 MPa.

The FC vessel is a pressure vessel comprising an ASTM A106 seamless pressure pipe (6” diameter, 39” length) to which two 15” diameter blind carbon steel weld neck flanges are attached. It is interesting to note that the steel pipe was manufactured in Brazil, the 9th largest crude steel producer (at 34.2 million tonnes in 2013) [51] and that (unsustainable and probably low yield) charcoal was used to fire the furnaces to create the steel. Both flanges are secured with 12 bolts made of threaded rod.

The bottom blind flange is held in place by the 12 bolts except during occasional repair of the heater or bottom parts and a 6” 304 stainless steel spiral-wound gasket (Flexitallic, API601, class 600) creates an airtight seal. The bottom flange has two holes drilled, which are tapped for National Pipe Thread (NPT); this is where the Swagelok connections are made. One of the holes is connected to a T-section leading to 0.95 cm (3/8") Swagelok lines and, eventually, the exhaust. The other opening accommodates the electric wires for the heating element inside the vessel. This element supplies heat for the carbonization reaction and consists of a flexible 2500 W Aerorod BXX ARI-branded heater, coiled to a diameter of 5 cm by the operators in the R3-Laboratory. The heating element is housed in a steel round casing (a regular pipe), which works as a support for the FC canister. In the past, the FC canister has knocked against the heating element during loading, causing it to deform, break and eventually burn out.

The upper flange includes 2.54 cm (1”) openings in the center, fitted with NPT to Swagelok and accommodating the 0.635 cm (0.25”) air inlet, 0.635 cm (0.25”) inlet for the TC inlets and 0.9525 cm (0.375”) pressure safety lines. The top flange is bolted in an airtight way to the carbon steel cylinder identical to the bottom flange. Depending on the skill of the operator (the bolts must be tightened in a crisscross sequence, three times with a ratcheting wrench), the upper flange can be considered as a quick-opening closure. The upper flange uses a Durlon gasket made of a mixture of aramid/inorganic fibers and nitrile rubber, which we try to re-use (rated to 371°C and with a sealability of 0.4 mL of nitrogen per hour). Carbon paste (Key Graphite Paste) is used both as a sealant (when hot, the paste expands, creating an even tighter seal) and a protectant for the gasket. The paste is thinned with warm water to the required thickness.

All lines are made of Swagelok tubes and connections. In general, all Swagelok air inlet lines
are 0.635 cm (0.25”) in diameter, while the lines that carry the exhaust (together with the safety lines) are either 0.9525 cm (0.375”) or 2.54 cm (1”). All these Swagelok lines are rated at 21.5 MPa (3100 psig) at 37°C, (down)rated 18.3MPa (2635 psig) at 300°C using ASTM A269. Figure 2.1 shows the most updated setup of the FC reactor as of 2015. To make the drawing clearer, all the lines that are not used in normal operation and are installed for safety (to the burst diaphragm, the spring loaded pop-off valve and the pneumatic valve) are shaded light green. The lines delivering air are colored blue. Looking closely, it becomes evident that the blue lines are thinner than the others; these are the 0.635 cm (0.25”) Swagelok lines, while normal lines are 0.9525 cm (0.375”). Close to the stack in the right upper corner of figure 2.1, the lines are one inch wide in diameter.
The FC pressure vessel is equipped with several safety systems to allow fast depressurization during an emergency. A pneumatically operated (with 100-150 psig of any inert gas, we like to use \( N_2 \)) ball valve is used to bypass the downdraft valve. The pneumatic system itself is activated by an internal relay built into a pressure digital readout (DP25-S Omega). Depending on the experiment, the set-point at which the pneumatic valve releases the pressure, changes. The pneumatic valve will, for example, lower the pressure by 0.45 MPa (50 psig) when the set-point is 2.17 MPa (300 psig).

The ultimate safety mechanism is the 1” carbon steel rupture disc holder that houses a burst
diaphragm from Oseco that is rated at 2.77 MPa (387 psig). This burst diaphragm is directly connected to the top of the reactor vessel. The lines connecting the rupture disc holder to the exhaust are wider (2.54 cm (1") instead of 0.9525 cm (0.375")) to allow fast depressurization.

Another pressure release mechanism is the spring-loaded relief valve manufactured by Crosby Valve & Gate (900 series), in which the valve seat is forced against the valve inlet nozzle by a factory-installed and calibrated spring. This valve is a remnant of a different operation mode of the FC unit. It has been left in place because it allows fast depressurization, as it is able to release gases fast into a 2.54 cm (1") Swagelok line. A CO alarm is attached beneath the exhaust, to warn operators if CO levels become too high.

Loading the FC vessel with biomass would not be very difficult, but when charcoal is made, it would be problematic to remove all the charcoal from the vessel. For this reason we use a removable stainless steel FC canister. Because the canister rests inside the vessel and does not need to hold any pressure, this piece of equipment can be easily altered by the $R^3$-staff. A typical canister is insulated with Kao wool, which is kept in place by stainless steel sheet metal and hose clamps. Recently, a thermocouple holder was made of perforated stainless steel tube and is kept in place in the canister by a spider, both at the bottom and top. The bottom of the canister is open to the atmosphere in the FC vessel by means of a stainless steel mesh. In figure 2.1, the reactor canister is shaded in darker grey and displayed as if it were already loaded in the FC vessel. At the bottom of the canister you notice the mesh. This mesh supports the loaded biomass and depending on the particle size of the biomass, a finer or coarser mesh can be used. The adjustment of the mesh to the particle size prevents particles, tars and ash getting into the exhaust lines, where they would cool down and cause clogs.

The top of the FC canister is sealed in an airtight way using a stainless steel lid with a diameter slightly larger than the canister. The seal between the FC canister lid and the FC canister itself is made by securing the lid with two allen drive socket caps to the cylinder via a custom-cut Flexitallic SF 2401 Aramide/Nitrile gasket, which has to be replaced regularly, depending on the severity and duration of the experiment. The two socket caps allow a steel cable to be connected to the FC canister, making it possible to lift the FC canister into the FC vessel by means of the 1 tonne hoist mounted on an I-bar on the $R^3$-Laboratory ceiling. In figure 2.1 the air supply is shaded in blue, making it easy to follow into the FC reactor. The FC canister is sealed in an airtight way because we want the supplied air to flow through the canister and not around it. The canister is connected directly to the air supply lines via a flexible Swagelok line (made of 316L convoluted stainless steel, reinforced with metal braid) via a Swagelok quick-connect.
This is an important feature of the FC reactor; the compressed air introduced in the reactor is forced onto the top of the biomass bed, making the FC apparatus a downdraft reactor. The lid’s 0.635 cm (0.25”) Swagelok line is long enough to stick out of the top flange, for easy insertion of several (0.1016 cm or 0.040” diameter) Omega type K sub-mini thermocouples into the FC canister and TC holder. Installing several thermocouples and creating an interface in a pressure vessel containing hot gases is complicated, but it was accomplished using a Conax-brand Teflon compression seal fitting. With the current configuration, up to eight thermocouples can be placed in the middle of any biomass bed at different heights. Experiments were carried out with different diameter canisters. A smaller diameter canister allows for (extra) Kao wool insulation to be installed, which might favor the production of charcoal because less heat is transferred to the 175 kg reactor vessel.

Table 2.1 shows the main differences between the two canisters (also see Figure 2.2), which both have a height of 97.5 cm. The outer diameters are 11.4 cm and 7.6 cm (4.5” and 3”) for the old and new canister, respectively. The IDs were measured with a dial caliper (which reads accurately to .001”) as 10.9 cm (4.29”) and 7.0 cm (2.77”), respectively. The decrease in cross section changes the area by a factor of 2.4, the flow rate of air should therefore be decreased by an equal amount, for equal superficial air speeds in both canisters.

Table 2.1. Main differences between the two lab-scale FC canisters.

<table>
<thead>
<tr>
<th></th>
<th>Small Canister</th>
<th>Large Canister</th>
</tr>
</thead>
<tbody>
<tr>
<td>OD [cm (”)]</td>
<td>7.6 (3)</td>
<td>11.4 (4.5)</td>
</tr>
<tr>
<td>ID [cm (”)]</td>
<td>7.0 (2.77)</td>
<td>10.9 (4.29)</td>
</tr>
<tr>
<td>Kao wool thickness [cm (”)]</td>
<td>Up to 2.5 (1)</td>
<td>Up to 0.635 (0.25)</td>
</tr>
<tr>
<td>Weight [kg]</td>
<td>7.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>

*aThe weight is measured with the top lid, gasket and of the canister included.
Figure 2.2. Main differences between the large canister (left) and small canister (right) are the diameter (red) and thickness of the Kao wool insulation (purple).

Table 2.1 shows the Kao wool thickness, which is not constant; Kao wool is prone to compression and with repeated use of the canister, the Kao wool becomes thinner. Over time, this might influence the insulation characteristics of the Kao wool, which will trap less air. Unlike the old canister, the new canister does not fit tightly into the vessel: there is some space between the Kao wool and the vessel. When the old canister is being loaded, it will touch the walls of the vessel from every side whereas this does not happen with the new canister. During operation, the Swagelok 0.635 cm (0.25") line (which houses the thermocouples) will force the canister to be centered within the vessel. Figure 2.3 illustrates the space between the canister and the vessel.
Standard Operation

During a typical FC experiment, compressed air was delivered from a 4-cylinder air-cart (made of Swagelok lines and scuba tanks) pressurized up to a maximum of 20.7 MPa (with the regulator set at 4.59 MPa (650 psig) for FC experiments). Air was used during FC experiments to pressurize the reactor and create combustion, thereby allowing pyrolysis. The flow rate of air was controlled by a Swagelok metering bellows-sealed valve connected between the air-cart and the FC reactor.

Power was supplied to the heating element by turning on a switch that ignites the feed loaded. A Powerstat 1296D variable auto-transformer (VariAC) steps down the AC input voltage to a preferred voltage (but can also boost the voltage to a higher level!). This 208 V is stepped down to 45%, unless otherwise noted. After ignition, the heater is turned off either after an arbitrarily determined six minutes, or when the pressure rose by more than 20 psig.

This supply of air sustains the combustion of the vapor phase of the feed, which in turn delivers the heat needed for pyrolysis, which takes place closer to the solid particles where oxygen deficiency occurs. Supply of air occurs on the top of the reactor (as this is a downdraft reactor), which forces the flame to move upwards through the feed. During operation, gases are released through a Bonney forge 1/2” 800 HL-31 downdraft valve to keep the pressure inside the FC reactor at a constant level. This valve is taken apart every other run, to check for deposits and possible particles that might occur.
prevent the valve from closing, and prevent the operator from reaching a certain pressure. The opening or closing of the downdraft valve to maintain a constant pressure, is an art form mastered by few. The lines exiting the FC reactor contain two condensate traps (one at atmospheric (ACT) and one at pressure (PCT) conditions; see Figure 2.1), which accumulate the tars and excess water during the FC experiment.

The endpoint of a typical FC experiment depends upon the feedstock used and its moisture content, as well as the air flow rate chosen. Carbonization of bana grass takes only 20 minutes, while the time needed to fully pyrolyse wet sewage sludge easily exceeds an hour. A useful parameter to decide the endpoint of an experiment is the Air-to-Biomass Ratio (ABR), which is a weight ratio of delivered air to the loaded dry biomass, and is defined as:

\[
ABR = \frac{M_{\text{delivered air}}}{M_{\text{dry feed}}}
\]  

(2.3)

The air initially present in a pressurized FC vessel is not included in the ABR calculated in equation 2.3. As the ABR is used frequently to "guesstimate" the endpoint of an FC experiment, it is not necessary to know the total ABR if comparing experiments conducted at the same initial pressure (and packing density). The \( M_{\text{delivered air}} \) is calculated using the pressure of the air-cart before and after an experiment. By using a value of 3.2 g/psig of air delivered (based on a previous research project by Greg Specht in the \( R^3 \)-Laboratory), the mass of air delivered can be calculated. To calculate an ABR for experiments that did not fully carbonize the biomass bed, the ABR was estimated by calculating the ABR for the part of the bed that was perfectly carbonized, and then adding the amount of extra air needed to carbonize the remaining feed.

A Catalytic After Burner (CAB) was used in advance to clean the gases in the effluent by combustion, especially for CO and particulate matter, but was disconnected at the very early stage of the sewage sludge work in this thesis. The CAB was filled with steel monolith and platinum catalyst, which was preheated above 300° C during experiments and supplied with secondary air from a six scuba tank air cart (instead of the four scuba tank air cart) to ensure combustion.

During an experiment, the temperatures and pressures (see figure 2.1 for locations) are measured with Omega Type K thermocouples, monitored and recorded with NI equipment using NI LabVIEW. Initially a 25-year-old NI SCXI-1000 equipped with a terminal block NI SCXI-1303 was used and connected via a Windows XP computer with a National Instruments Type II PC card (DAQcard-6062E). Later in the experiments, the data acquisition system was replaced with a 2014 NI Compact-DAQ 9178, equipped with a NI 9214 16-Channel Isothermal module for the thermocouples. The electrical signals from the pressure transducer (Omega PX602-5KGV, rated at 51.8 MPa (7500 psig)) were recorded using a NI 9205 32-Channel analog input module. The NI 9214 has superior noise
cancelling characteristics compared to the NI 9205 (the electrical signals generated in the thermocouples are also much lower than the +/- 100 mV signals from the pressure transducers), and it was decided to use the 9214 module to record both temperatures and pressures.

Although digitalization and labVIEW both offer important advantages, an analog pressure gauge (Omega, 1000 psig) is nonetheless used to monitor the pressure in the FC vessel. The computer is connected to a battery pack in case of a power out, and handheld digital thermocouple readouts are kept within reach.

**How to act like a charcoal expert**

One of the biggest advantages of the FC process is that it allows the operator to manufacture charcoal at very large yields. The charcoal yield allows for an (economical) comparison of different charcoal processes, providing insight into how much feed is needed to create a given amount of charcoal.

Some processes used in developing countries to make charcoal, such as earth pits or mounds, barely achieve charcoal yields of 15% [52], while newer (and continuous) processes like the Lambiotte retort or ACESITA carbonizer [53] reach 36%. The formula on the left shows the formula to calculate the charcoal yield on a dry basis. The right formula is the charcoal yield when part of the charcoal in the reactor is not fully carbonized. We may subtract the amount of uncarbonized feed, because it is fair to assume that we will carbonize this feed in the next FC run.

\[
y_{\text{charcoal}} = \frac{M_{\text{charcoal}}}{M_{\text{feed}}} \quad (2.4)
\]

\[
y_{\text{charcoal}} \approx \frac{M_{\text{charcoal}}}{M_{\text{feed}} - M_{\text{uncarbonized feed}}} \quad (2.5)
\]

However, before beginning carbonization, it is important to know the exact moisture content of the type of biomass we are dealing with. Biomass is wet, and its moisture content will vary from day to day. Freshly cut wood typically has a moisture content above 60%, wet basis (wb) while sewage sludge can have moisture contents over 90%, wb. Typically, if enough time is given, biomass will equilibrate to a moisture content of 10%, wb in the \(R^3\)-Laboratory. By reporting on a dry basis, comparison between different feedstocks is possible.

The moisture content (MC) can either be reported on a dry or on a wet basis. When reporting on a dry basis, moisture contents of over 100% can be obtained, which is not intuitive. Therefore, this thesis will consider only wet basis.
\[
MC_{\text{wet basis}} = \frac{M_{\text{initial}} - M_{\text{after drying}}}{M_{\text{initial}}} \quad (2.6)
\]
\[
MC_{\text{dry basis}} = \frac{M_{\text{initial}} - M_{\text{after drying}}}{M_{\text{after drying}}} \quad (2.7)
\]

For the above-mentioned calculations, certain standards (ASTM) can be followed, which differ slightly from one another depending on the type of sample feedstock. Each chapter in this work will discuss the ASTM used. In general, a small sample is taken from the feedstock, and dried till no mass loss occurs between consecutive drying periods in an oven at 105°C. It is imperative to minimize the time between weighing a sample and analyzing its moisture content. During a long-drawn-out period between weighing and analyzing, the sample might gain or lose moisture, rendering the calculated charcoal yields useless. A Mettler Toledo MS204S electronic scale is used with an accuracy of 0.1 mg.

Real charcoal professionals do not brag about charcoal yields, but use fixed-carbon yields. The fixed-carbon yield tells exactly how efficient the charcoal is made. Over the past four years in the \textit{R}^3-Laboratory I have repeatedly come across the following papers [6], [54], [16] and [36] which explain the vague and very misleading definition of charcoal yield.

The only time that it would be correct to use charcoal yield in comparisons is when the charcoals all have the exact same composition in terms of proximate analysis. The yield proposed by [6], [54], [16] and [36], which incorporates the composition of the charcoal in the yield is the \(fC\) yield calculated on a dry ash free basis.

\[
y_{fC} = y_{\text{charcoal}} \times \frac{\%fC}{100 - \%\text{feed ash}} \quad (2.8)
\]

To obtain the \(\%fC\) in the formula above, we need a drying oven at 105°C, a furnace capable of reaching temperatures up to 950°C, high temperature resistant crucibles, a 0.1 mg accurate scale and an alert operator. The proximate analysis is not so approximate as some people might think. The proximate analysis is the backbone of the \textit{R}^3-Laboratory. After each experiment, among the first things to determine is the quality of the charcoal just produced, which is what the proximate analysis offers. Historically, coals have been classified using the proximate analysis principles.

The proximate analysis determines the fixed carbon (fC), volatile matter (VM), MC and ash content of a charcoal; we follow the ASTM standards for wood charcoal (Standard test method for the chemical analysis of wood charcoal: D1762-84). The standard allows us (and other laboratories)
to determine the fC content of a charcoal and compare it. If an operator decides to change some of the steps, comparison is no longer possible.

Air-dry charcoal must be ground with either a mill or by hand with mortar and pestal. If mill-ground, the operator should exercise care not to grind the sample too long, as the mill might heat up and prematurely devolatilize the sample. One gram (to the nearest 0.1 mg) of ground charcoal is weighed and loaded into a porcelain crucible that has been prefired at 750°C in a muffle furnace (Thermolyne 1300 furnace or Thermo Scientific 1400 in the R3-Laboratory) for 10 minutes with one hour cooling in a dessicator. This prefiring functions as a cleaning step, and also tempers the crucibles for thermal shock in later stages of the proximate analysis. We like to use a maximum of 3 crucibles per proximate analysis, loading them with charcoal particles that pass through a No. 20 sieve (850 µm).

The moisture content is analyzed by loading the charcoal and crucibles (with lid, but not covered) in a vacuum-oven at 105°C for 2 hours followed by one hour of cooling in a desiccator. After cooling, the dry charcoal samples are weighed, and the drying procedure repeated, with 1 hour heating, and 1 hour cooling until the mass difference between two weightings is 0.5 mg or less.

The volatile matter determination procedure is prone to errors, and timing is crucial. During the moisture content step, all the water of the sample should have escaped the charcoal sample. The (now) oven-dry charcoal and covered crucibles are placed in a muffle furnace preheated to 950°C using the following timing sequence: the covered crucibles are placed on the outer ledge of the open furnace door for two minutes, then on the edge of the furnace for three minutes, and inside the closed muffle furnace for six minutes. This allows the charcoal to devolatilize slowly without causing the temperature to increase so quickly that it ignites the escaping gases. Combustion will create turbulence and might pull particles in its draft. The charcoal and crucibles are cooled down in a desiccator for one hour and weighed. The volatile matter weight percentage is calculated as follows:

\[
\%VM = \frac{M_{\text{oven-dry charcoal}} - M_{\text{after 950}}}{M_{\text{oven-dry charcoal}}} \tag{2.9}
\]

The ash content is anything that remains of the charcoal after placing the uncovered crucibles in the muffle furnace at 750°C for six hours followed by a one hour cool-down in a desiccator. This procedure is repeated with one hour heating and one hour cool-down until a mass difference of 0.5 mg or less is observed. The ash weight percentage is calculated as follows:
\[
\% Ash = \frac{M_{\text{residue}}}{M_{\text{ooven-dry charcoal}}}
\] (2.10)

The difference between the VM content and the ash content is the fC content, i.e. the amount of charcoal burned off during the ashing procedure.

The fC weight percentage is calculated as a difference as follows:

\[
\% fC = 100\% - \% Ash - \% VM
\] (2.11)

The proximate analysis can also tell us if something is really a charcoal. Typically, a charcoal is considered to have a VM content of less than 30\% and preferably a low ash content. Figure 2.4, below, shows the fC, VM and ash content displayed on a ternary plot, and demonstrates when a charcoal can be considered to be a 'real' charcoal.

![Ternary plot fC, VM and Ash content to determine charcoal quality.](image)

Figure 2.4 displays proximate analysis data from the sewage sludge work (see Subsection 2.2.2 in this chapter), proximate analysis data from oak and sweet gum feed and charcoal [1] to show the
difference between feed and charcoal, proximate analysis of different types of commercial charcoals available, proximate analysis data from the macadamia nut shell charcoal discussed in section 2.3 and proximate analysis data from the carbonized Norwegian wood (see section 2.2.3).

The ternary plot is divided into a section having a larger and one having a smaller than 30% VM content. Charcoal typically has VM contents lower than 30%. Based on the literature [16], also data on the quality of a domestic charcoal and metallurgical charcoal is shown.

2.2.2 Biochar, black gold or just a hype?

As of today, it is still unclear how the properties of biochar, which is the modern version of the terra preta de indio, impact plant yields. There have been reports of 400% increases in maize yields in Zambia [55], but also negative effects [56] and temporary positive effects [57] have been observed. Better collaboration is needed between the biochar (or charcoal) manufacturers and the field scientists, to understand which type(s) of biochar will grow larger plants and under what conditions [58]. Only when this link can be made, will a successful implementation of biochar as a soil amendment be possible.

Probably the longest and most successful biochar to date was made by pre-Columbian inhabitants in the Amazonia. It is still unclear whether they made the terra preta de indio soils intentionally, or if it was a purely serendipitous occurrence, but what is certain is that the most fertile soils in the world existed in the Upper Xingu region and in Central Amazonia between 550 and 1640 Anno Domini (AD) [59]. The terra preta recipe from the Amazonia included bones and other waste materials as nutrient inputs. Some researchers even postulate that charcoal aficionado earthworms [60] were responsible for the high quality. Other, fewer, dark terra preta soils have been found in Amazonian parts of Peru, Columbia and southern Venezuela and in the Guianas.

The humid tropics are known to exhibit very low nutrient holding capacity and for the past 100 years, these dark soils have been considered as a way to enhance agriculture in poor soil conditions. But only recently has biochar become a scientific hype [61] [62] [63], partly due to the fact that, with the growing global population, we need environmentally sustainable ways in producing food [64].

Nordic dark soils have been found in the Northern region of Germany, and it is postulated that these soils, which, like the terra preta de indio, were a mix of organic waste, fecal material and charred biomass, were a cornerstone of the lives of the Viking-Slavic people in the 9th and 10th centuries AD [65]. In Australia, small patches of dark soil made by the campside of pre-European aboriginals, who must have deposited charred cooking residues and refuse, were found. These small patches of soils were named terra preta australis, after their bigger brother, the terra preta de indio [66]. Other well-known ways of improving soil quality are the European slash and burn techniques (with typically very low biochar yields) during the early and late Neolithic periods [67]. These
dark soils show the possibility of long-term CO$_2$ sequestration due to their incredible stability [68], hence the popularity in today’s global climate change debate. The optimal biochar has not yet been found, despite the large amounts of tests conducted. Great effort has been put in outlining the conditions needed to get a biochar that retains water and nutrients well and that has superior liming effects, but the link to agriculture is still missing [43]. The needed application rate for biochar depends on the specific soil type, the crop itself and the desired crop management.

**Sewage sludge carbonization research projects, a survey**

Biochar can be made out of waste material such as sewage sludge, which might seem like a win-win situation. Sewage sludge is waste with a disposal cost (over $100/tonne in the state of Hawaii), and after making biochar you potentially have a valuable product that is sterile, more homogeneous and stable compared to its original feedstock. More than 40% of today’s food was only possible because of mineral fertilizers [69], and mineral phosphate rock [70] is expected to deplete within a couple decades. Sewage sludge could be the long-awaited feedstock for biochar production as it consists of considerable amounts of N and P.

Not many people have a chance to write two theses. In my previous work (Ghent master thesis), I researched the sewage sludge situation, creating and communicating as if it were a 2011 snapshot. Four years on, I have had the opportunity to once again assess the sewage sludge situation in the world.

Eurostat states that 27.6 million tonnes of sludge were generated in the 28 European states in 2012. This is in contrast with 8.8 million tonnes in 2004 (and 6.5 million tonnes in 1991). Turkey, Germany and France are the top 3 producers with 10.1, 3.7 and 3.4 million tonnes, respectively [71]. This is much higher than the previously postulated 8.8 million tonnes of dry sewage sludge, partly due to the inclusion of Turkey’s sewage sludge production.

For most countries, the amount of sewage sludge generated has increased: for example, Belgium generated 118,000 tonnes of sewage sludge in 2002, which rose to 176,000 tonnes in 2010). Increases are to be expected as more people are connected to the wastewater system, and discharge thresholds of pollutants are ever-decreasing [72]. It is interesting to note the decrease in sewage sludge generated in the United Kingdom, which might be caused by extensive anaerobic digestion practices (more than 75% of all sewage sludges get digested), where the amount of sewage sludge is reduced during biogas production.
The $R^3$-Laboratory has been at the forefront of sewage sludge carbonization since 1982 [73]. In 2009 a paper by Takuya and Antal [47] in Energy & Fuels was submitted. The researched sewage sludge originated from the Ewa side of the island of Oahu, and was carbonized into charcoal using the $R^3$-Laboratory Flash Carbonization reactor. Sewage sludge charcoal is classified as low-quality according to the proximate analysis. As referred to above (see Figure 2.4), sewage sludge has a too low fC and a too high ash content to be useful in energy or other production applications. Possibly, the use of sewage sludge on land is deemed to be appropriate.

The key outcomes of the paper by Takuya and Antal were:

- It is possible to carbonize sewage sludge in the FC lab scale reactor.
- The charcoal yield decreases with increasing moisture content of the sewage sludge fed into the reactor. The maximum moisture content was 30%,wb.
- As, Hg ,Cd and Se are prone to elutriate from the reactor into the environment.
- Sewage sludge from the Ewa Waste Water Treatment Plant (WWTP) carbonized with the FC reactor is permitted to be put on land according to US EPA 40 CFR Part 503. Out of curiosity, we checked out whether the heavy metal concentrations were within permissible levels according to the State of Hawaii law and European legislation as well as the stricter Belgian regulations, and they were.

In 2011, the sewage sludge carbonization project was continued with a master thesis project (Ghent master thesis), and sewage sludge this time was collected at the Hawaii Kai (East Oahu) sewage sludge facility, operated by American Water, rather than from the Ewa sewage sludge facility. Both sewage sludges originate from residential waste water and from the same island. Figure 2.5 shows the approximate service areas of the Ewa (Honouliuli) WWTP in orange and the Hawaii Kai (East Honolulu) WWTP in red.
The Ghent master thesis objectives were threefold: (1) to investigate whether Hawaii Kai sewage sludge is at least equally adequate as a feedstock for the pressurized flash carbonization vessel; (2) to determine how efficiently (in terms of air delivery or ABR, and in terms of charcoal and fC yield) a sewage sludge charcoal can be made and determine the functional dependence of ABR on the moisture content of the sewage sludge feed, (3) to investigate how sewage sludge charcoal can be used in society: is it permissible to put these charcoals (or biochars) on land according to prevailing regional regulations. What happens to the heavy metals during flash carbonization?

The take-home messages of the Ghent master thesis project were as follows:

- It was observed that an insulated inside canister (which contains the sewage sludge) shows a decreasing trend of yields with increasing moisture content. This trend disappears when the insulation is removed. No general consensus of the effect of moisture content on yields was decided.

- Two sewage sludge feeds and two sewage sludge charcoal samples were sent out for heavy metal and elemental analysis. The corncob tinder feed and charcoal were also analyzed. A
high variability of heavy metals between the two samples (with a one month time-lapse) was observed. 53% of the organic sulfur and 86% of the nitrogen of the sewage sludge ended up in the gas-phase after flash carbonization.

- Neither sewage sludge feed sample could be put on land because of current regulations in the USA, HI, or Belgium, due to too high concentrations of As, Cu and Zn. Neither charcoal sample could be put on land because of too high concentrations of Cd, Cu, Zn, Ni, Cr and Mo.

The Ghent master thesis provided a good basis for a subsequent publication (and a third sewage sludge paper for the \(R^3\)-Laboratory) on the carbonization of sewage sludge: Sewage Sludge Carbonization for Biochar Applications. Fate of Heavy Metals [48] which is included in appendix B.

**Rectifying a few shortcomings**

Before the Ghent master thesis was publishable, additional research work was necessary. The Ghent master thesis lacked reproducibility between the different FC experiments. In addition, charcoal from only two FC experiments (1 and 2 in recent paper for SS1 and SS2, respectively) was selected to be sent out to an external laboratory - Hazen Research. More samples should be analyzed by different laboratories.

For the new sewage sludge publication (see appendix B), an additional six experiments were conducted at duplicate conditions. During the FC experiments for the Ghent master thesis, the amount of sewage sludge loaded in the reactor was not kept constant. The reproduction experiments carried out at the \(R^3\)-Laboratory for the publication all used 1 kg of sewage sludge at the lab equilibrium moisture content of 10%, wb. The series of experiments done for the sewage sludge publication made it possible to sample carbonization gases that condense out in the lines and collect in two different sumps. These liquids were carefully collected in the aforementioned lines and sumps (PCT, which was cleaned with a 10% volume basis NaOH solution with de-ionized water rinse before every experiment). For the additional sewage sludge FC experiments carried out for this publication, corncob was deposited on top of the sewage sludge bed (in addition to corncob tinder right on top of the heater and under the sewage sludge feed). The corncob functioned as a buffer layer, allowing the FC to be stopped in a timely manner, to ensure that the flame front moved through the sewage sludge bed, but would not consume the produced charcoal by combustion.

Additional analysis of the heavy metals has allowed a better prediction of how the heavy metals will behave during flash carbonization. The concentration of heavy metals entering the reactor through the feed (via sewage sludge and negligible amount in corncob in mg/kg of feed), the amount of heavy metals remaining/being absorbed in the sewage sludge and corncob charcoal in mg/kg of
charcoal, and the amount of the heavy metals that volatilize and condense with the liquids in mg/kg of liquid are all known. This will give an idea of which heavy metals will volatilize and escape the reactor in the gaseous phase or entrained on particles through the stack, since the sampling of heavy metals in an exhaust fume is not a straightforward task. In addition, the pooling of the condensates now gives us an internal control, as this sample was sent out to three different, certified analytical laboratories (Hazen Research, TestAmerica Laboratories, and FQ Labs) to detect heavy metal concentrations. In addition to the concept of depletion ratios used in the paper by Takuya and Antal, the idea of uptake ratios was explored in this publication. Depletion ratios show the reader how much of a certain heavy metal left the loaded feed in the FC reactor, while corncob charcoal uptake ratios quantified the fraction of heavy metals from sewage sludge that were captured by the corncob char.

In the first publication (by Takuya et al [47]) concerning sewage sludge carbonization, the concentrations of heavy metals in the sewage sludge charcoal were compared to the pollutant limits indicated by 503 CFR 404. If the concentrations are below these limits, unlimited loading rates of the sewage sludge charcoal are permitted. If these limits are exceeded, but the concentration of heavy metal falls below the concentration ceilings, restricted use is allowed. If the heavy metal concentration is above the ceiling limit, no addition of the charcoal to the land is allowed. The European Union has only one set of concentration limits, and all sewage sludge charcoal additions are limited on a mass per year per area basis. In the first publication, the heavy metal concentrations were below the pollutant limits, so no attention was paid to USA loading rates. For the second publication (see appendix B) on sewage sludge carbonization [48], some of its heavy metal concentrations in the charcoal were higher than the pollutant limits, but lower than the ceiling limit. The loading rate is either calculated using Annual Pollutant Loading Rates (APLR) in kg/ha/year or Cumulative Pollutant Loading Rates (CPLR) in kg/ha and the decision of which to use depends on whether the charcoal is sold in bags or in bulk, respectively. APLR would be more directed towards private use, where tracking for CPLR would be too difficult.

**Difficulties during the writing of the paper**

For the Ghent master thesis, the preferred analytical laboratory was Hazen Research. Additional heavy metal concentration analyses were needed for the new publication (appendix B), and supplementary sewage sludge feed and charcoal samples were sent to Hazen Research, FQ Labs, TestAmerica Laboratories, Laboratory of Analytical Chemistry and Applied Ecochemistry, the Faculty of Bioscience Engineering, Ghent University, and the Agricultural Diagnostic Service Center (ADSC), College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa. During preliminary screening of the heavy metal concentration results (especially Hg), ADSC was considered to have reported wrong results and its data was not used any further.
Figure 2.6 shows the average heavy metal concentrations of the pooled condensates sample sent out to the three different laboratories. The error bars (standard deviation from the average) are shown and are possibly bigger for the heavy metals As, Cd, Pb and Hg, as the upper limits for those concentrations were used. Since the sample sent out to the laboratories was assumed to be homogeneous and thus well mixed, the cause of the variations must lie elsewhere.

The most crucial step which varies between laboratories (in fact unknown to us) is the digestion of the heavy metals, along with the apparatus used for the detection of heavy metals. Before analysis can be carried out, the heavy metals must be dissolved in an aqueous solution. Each laboratory has its own set of standards, while others even adjust official standards. The heavy metal concentrations that we discuss in this publication found in appendix B are total heavy metal concentrations, and depending on the severeness of each laboratory’s standard, we will observe higher or lower heavy metal concentrations.
We would like to conclude the sewage sludge work done at the \textit{R}^{3}-Laboratory with the following take-home messages included in a recent publication of which I am first author (see appendix B):

- The flash carbonizer lab reactor operates under such conditions that make Hg, and to a lesser extent As, Cd, and Se go to the gas phase and leave the reactor.

- A wide range of fixed carbon yields are obtained (from 9%-28.6%)

- There is a large spatial and temporal variability in the heavy metal concentrations on the island of Oahu.

- Hawaii State and Belgian law does not allow us to put Hawaii Kai sewage sludge charcoal on land, while restrictions apply on a US federal level. The restrictions are due to Zn, Mo, Cr and Cd, Cu, Ni, Zn for the state of Hawaii and Belgium, respectively.

- Other disposal methods of Hawaii Kai sewage sludge charcoal than land application should be examined.

Water conservation strategies are causing a decline in water use in the US, but as the heavy metal pollution stays constant (or even increases), the waste waters and their sewage sludges will have higher concentrations of heavy metals. This will make the flash carbonization of sewage sludge only more problematic regarding land application as a fertilizer or soil remediation commodity as certain heavy metals tend to upconcentrate in the biochar.

There has been interest in removing nitrogen [74] and phosphorus [70] from sewage sludge so as to be put to use as raw materials. The interest in removing heavy metals to be re-used and sold as pure metal is a new idea [75]. Westerhoff et al estimated values of $280 per tonne of sewage sludge because of the intrinsic value of the present metals. The economic feasability of the metal recovery is being evaluated.

Table 2.2 displays the value in $ per kg of dry sewage sludge (for SS raw) or dry biochar (for SS biochar). The object of our analysis of Experiment 2 in the sewage sludge paper [48] are the heavy metal concentrations of the raw sewage sludge and the sewage sludge biochar. Experiment 2 is chosen because it exhibited the largest fixed carbon yields. The profits are calculated by using the total amount of sewage sludge produced on the island of Oahu in 2006 (40,000,000 metric tonnes). It is only because of the Cu, that the removal of heavy metals is considered to be profitable. The prices for each heavy metal can be traced online at infomine.com.
If the heavy metals are extracted from the sewage sludge biochar, the profits would get close to the profits generated by raw sewage sludge extraction, as the charcoal yield is very high using the lab-scale flash carbonization apparatus. On top of this, after heavy metals have been extracted from the sludge, the sludge must still be thermally (or chemically) treated before it can put on land. The profits that can be made in a year’s time (over a million dollar!) are a mere estimate, as the metal speciation (physical-chemical form: ionic/colloidal/particulate) will play a crucial role in the recovery efficiency, and when a metal is extracted by pyrolysis, electrolysis, chemical precipitation, bio leaching, acid digestion (similar to the digestion done by analytical laboratories like Huffman and Hazen) or any other technique, it needs conversion into a usable form, which will require additional costs.
2.2.3 Charcoal ’mines’ in the Norwegian woods

Why are we interested in Norwegian wood charcoal?

Because of the increasing demand for (Si-based) solar panels, for computer chips (following Moore’s law), and for silicon for the massive metal production of countries like China [76], the demand for silicon alloys and other ferroalloys has never been higher. The metal and alloy industry heavily depends on coal as a raw product. In electric arc furnaces, coal acts as a reductant and a carbon source, while in the older blast furnaces coal also acts as an energy source.

These industries will not face raw silicon shortages, because over 25% of the earth’s crust consists of this element, usually found in the form of silica $SiO_2$. However, justifying the use of coal as a raw product in the manufacturing process of computer chips, photovoltaic panels and other metal commodities will pose a problem, especially with changing climate change policies.

There are not many substitutes for coal, but charcoal is one. Charcoal has low ash and sulfur content compared to coal, while still maintaining high SiO reactivity, which makes charcoal the most favorable reductant for Brazil and Norway. Arguments against charcoal are that it is very fragile, ignites easily at low temperatures, and can show hygroscopic characteristics in humid environments [77].

Charcoal was the preferred reducing agent for blacksmiths in the Middle Ages [31], but was gradually replaced by coal despite charcoal’s above-mentioned superior characteristics. In 1901, it was still common to use charcoal rather than coal to make ferrosilicons with a purity of 75% and higher [78]. Later in the 20th century the switch to coal was easy because of its accessibility and low price.

Since 1980, Brazil has been replacing coal with charcoal in metal manufacturing, and its demand for charcoal soon tripled (Brazil used to be the lowest cost steel producer in the world [19]), causing massive deforestation and $CO_2$ emissions [20]. The combination of enormous lignocellulosic resources (the Amazonian rain forest in Brazil covers more than 5,500,000 $km^2$), and lax deforestation rules have resulted in over 50% of Brazilian charcoal originating from native forests [79].

The second issue with switching to charcoal is the cost. So far, countries such as Malaysia, Brazil, Argentina and recently Norway (specifically its major ferrosilicon industry) use charcoal as a reductant, but they are investigating the cost issues. Charcoal is not cheap: various papers report prices between 162 and 780 $/tonne [33]. The coal price in the US in 2013 lies between 10-60 $/tonne, depending on the grade of coal [34].
In all, 77% of the world's silicon production (which totals 7,680,000 metric tonnes) is used in the ferrosilicon industry. The four leading ferrosilicon and silicon metal producing countries are China (65%), Russia, Norway and the US.

Norway, for example, produced 369,000 metric tonne in 2015 [80]. The silicon production industry of Norway had a world’s share of 9% in 2012. Norway is also one of the world’s main exporters of ferrosilicon and ferromanganese [81]) with a share of 4% [82].

A quick calculation provides an excellent illustration of the issues:

The equation for carbothermic reduction of silica into silicon is shown below:

\[ \text{SiO}_2 + 2C \rightarrow \text{Si} + 2\text{CO} \]  

(2.12)

0.86 kg of carbon is needed to manufacture one kg of silicon. Charcoal is not pure carbon; typically it contains 70% carbon, thus requiring 1.23 kg of charcoal to manufacture 1 kg of silicon.

Producing 369,000 metric tonnes of silicon per year takes 453,870 metric tonnes of charcoal. Assuming a carbonization with a modest yield of 25% is used, in total 1,815,480 metric tonnes of dry wood are needed. We will avoid transportation from e.g. Indonesia which would double the charcoal cost [83] so in this example we investigate the manufacturing of charcoal from Norwegian wood.

Norway has a standing forest of 765 million m$^3$, which increases each year by 25 million m$^3$. Of this growing stock, approximately 10 million m$^3$ will be harvested for all industries (paper, fuel wood, etc.).

The density of (Norwegian spruce) wood varies greatly over individual trees and even over the various parts of the same tree [84], so an average of 600 kg of freshly cut wood/m$^3$ will be used.

Only two-thirds of a tree will be hauled to a processing factory [85]; this freshly cut wood typically contains over 2 kg of water for every kg of wood. The amount of dry wood available for further processing in Norway adds up to:

\[
\text{Dry wood available} = 10,000,000 \text{m}^3 \times 600 \frac{\text{kg wet wood}}{\text{m}^3} \times \frac{2}{3} \times 0.33 \frac{\text{kg dry wood}}{\text{kg wet wood}}
\]

(2.13)

So that:

\[
\text{Dry wood available} = 1,320,000 \text{ metric tonnes}
\]

(2.14)

Using the whole tree (and all forest residues) brings us closer to the amount of tonnage needed to supply ONLY the ferrosilicon industry in Norway.

33
Flash carbonization may be a fast and economical way to use Norwegian birch or spruce - or even their forest residues - to make the fixed-carbon charcoal necessary for the ferrosilicon industry. This is part of a four year BioCarb+ project which tries to find new technologies and ways to produce a valuable charcoal from waste material. In the following section, we explain the inherit characteristics of hardwoods such as birch and softwoods such as spruce, and provide an overview of the pyrolysis of hard and softwoods found in the literature.

**Hardwoods or Softwoods or both?**

Since 1990, European forests have, partly as a result of afforestation, increased in surface area by more than 17 million hectares. The European forests cover some 180 million ha, accounting for 40% of Europe’s land mass [86]. Countries like Finland and Sweden have a forest and tree cover of 76% [87] and up to 80% of Finland’s energy comes out of biomass. In the US, only a mere 11% of the total wood harvested is used as fuel [88]. Figure 2.7 shows the use of wood in the European Union, revealing that almost 50% of the total volume of wood is used for energy purposes. The use of wood, including forestry waste, for energy purposes has been increasing for the last ten years [89] with Sweden and Finland on top.

![Figure 2.7. Wood resources use in the European Union. Source: [3].](image)

In the previous section we pointed out that considerable amounts of wood are needed to provide for Norway’s ferrosilicon charcoal needs. There are vast amounts of forest biomass readily available but caution is needed in not trying to copy what the Brazilian steel industry did in the Amazon, or what happened in Iceland some 200 years ago. The production of birch charcoal in the
metallurgical industry was partly responsible for the huge deforestation of Iceland between 1587 and 1870 [90]. Similar to Iceland, Uzbekistan now has to import large amounts of birch charcoal to keep manufacturing over 18,000 tonnes of silicon a year [91].

Norwegian spruce makes up 45% of the forest in Norway, being the dominant type of wood [92]. The birch tree is native to Northern Europe and the most common hardwood in Norway at 16% of the forest [92]. The extractive-rich bark of the birch tree is used in Sweden to make bread [93] and refreshing drinks [94]. Iceland turns it into a sweet liqueur named *Birkir* or *Bjork*, believed to benefit skin and hair.

Forest residues or GROT (an acronym for *GRenar Och Toppar*, i.e. branches and tops) are a very attractive biomass resource. These residues, consisting of limbs, tops, and unmarketable stems, are produced during thinning or partial cuts and in final forest harvests [95]. This type of residue is Norway’s most abundant and probably cheapest biomass resource, being available year round, in contrast to agricultural biomass. Currently 20% of all residues in Sweden are used as an energy source [96].

Bioenergy production from forest harvest residues, with a view to displacing carbon emissions from fossil fuels, will admittedly still be attended by CO$_2$ emissions. But if forest residues are left behind, fossil fuels will still be used and the carbon in the residues will be emitted little by little into the atmosphere as a result of decomposition anyway. Opponents of forest residue usage are concerned that excessive removal of forest residues is likely to ultimately entail nutrient imbalances and, as a matter of consequence, reduced forest productivity [97]. Forest residues typically contain more ash and extractives because of the presence of the needles and bark [98]. These residues are richer in nitrogen compounds [99] and are very heterogeneous in texture and chemical composition. The chemical differences between softwood spruce, hardwood birch and their GROTs are likely to have an effect on product distribution and fixed carbon yields during pyrolysis.

Both soft and hardwoods have very similar cellulose contents (42 and 44%) [100]. Birch wood contains 22% lignin, which is less compared to spruce, and 23% of hemicellulose, which is more compared to spruce [101]. In addition to higher lignin contents [102], conifers such as spruce also possess large amounts of extractives, resulting in a higher energy content [103]. That is why lignin and extractive-rich bark and branches of softwoods have a higher calorific value than stem wood [104]. These extractives are a complex mixture of low molecular weight sugars, inositols, amino acids, simple fats, carboxylic acids, terpenes, and phenolic compounds [98]. Extractive-free wood possibly favors char and gas yields during pyrolysis [102]. Furthermore, hardwoods typically have higher densities compared to softwoods, and external factors like silviculture practices can alter
density [105]. The main biomass constituent that favors char formation was found to be lignin [102]. This was confirmed by a Thermo Gravimetric Analyzer (TGA) (which in a sense, is a kind of carbonizer) kinetic study in which the highest charcoal yields (23% for spruce and 26.5% for redwood) were found in softwoods rather than in hardwoods [106].

Birch [107] and spruce [108] wood carbonization offers other advantages, in that the aqueous phase of the condensates contains acetic acid and furfurals which could be useful in the biological pesticide industry or as a wood preservative.

Up to 82% fixed carbon contents of birch charcoal with ash contents of 1.4% have been achieved by Fagernas et al [107], while in another publication [109], 79.6% fixed carbon birch charcoal was made with a charcoal yield of 34%. If we apply our formula (equation 2.8) and use their ash content (0.6%), a fixed carbon yield of 27.2% is calculated. In a comparison between torrefaction characteristics of Norwegian spruce and birch, birch was found to be more reactive compared to spruce. The birch also exhibited large devolatilization rates together with lower solid (no charcoal!) yields [110].

Liang et al [111] evaluated the effect of sample size and pressure on the fixed carbon yields of spruce wood and GROT by using atmospheric and pressurized TGA’s. The fixed carbon yield increased from 18.94 to 30.86% when the pressure was raised to 0.8 MPa. The highest fixed carbon yield for the GROT was found at 0.8 MPa with 29.85%. The following Table 2.3 gives the proximate analysis of spruce wood and GROT obtained by Liang et al on the basis of the same feedstock as the one used in this work. Surprisingly, the GROT has higher fC contents compared to the wood, but as expected, larger ash contents.

<table>
<thead>
<tr>
<th>Table 2.3. Proximate analysis of spruce wood used in previous and present work.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis</td>
</tr>
<tr>
<td>VM fC Ash</td>
</tr>
<tr>
<td>%, db</td>
</tr>
<tr>
<td>Spruce wood 83.43 16.01 0.56</td>
</tr>
<tr>
<td>Spruce GROT 76.84 20.66 2.50</td>
</tr>
</tbody>
</table>

It is worth mentioning, particularly as we are confronted with the same heavy metal issue in our treatment of sewage sludge, that wood ashes might contain trace amounts of heavy metals.
When comparing birch and spruce, Pb and Zn are most enriched in birch wood ashes, while Ag is relatively enriched in spruce wood ashes with median lead concentrations of 516 mg/kg median, peaking to 1460 sometimes and Zn 14,600 mg/kg for birch. The maximum concentrations of Cd are also amazingly high in both birch and spruce wood ashes: 203 mg/kg and 184 mg/kg respectively. Zinc reaches a maximum concentration of 7910 mg/kg in spruce wood ashes [112] which is almost three times higher than the sewage sludge biochar Zn concentration from the publication [48]. Note has to be taken that the comparison between ashes and charcoal is not straightforward.

**Experimental Procedure**

The Norwegian spruce and birch wood that we used in our experiments had an initial moisture content of over 50% and 43%-45% (branches and stump) respectively after harvesting in Southern Norway in September 2014. The tree was taken apart into branches, stem and roots and chipped with a Heizohack HM 8 500 drum chipper, and oven-dried at 105°C for 72 hours before being sent to the R³-Laboratory. The tree stump was washed before chipping to avoid contamination with soil particles.

Typically, birch has a lower moisture content than spruce [113] (with a maximum of 50% and 60%, respectively) and spruce has a larger ash content in every part of the tree compared to birch (with a maximum of 3.20% and 2.18%, respectively).

The Norwegian spruce was delivered in February 2015. The Norwegian birch and spruce wood and spruce and birch GROT were delivered in March 2015. All the Norwegian woods were equilibrated to the R³-Laboratory conditions in a fume hood for at least a week prior to any experiments, to render the moisture content of the wood uniform across the sample. The moisture content was analyzed prior to every experiment using ASTM E 1756 Method A, the results of which can be found in Table 2.4. The ASTM standard requires the use of small (0.5 g) samples to determine MC. Tests were done to see if larger samples (8 g was used) would translate into different, i.e. more correct MC values, as the sample would then be more representative. However, this was not the case and the wood was assumed to be uniform in moisture content. The following Figures 2.8, 2.9, 2.8 and 2.10 show all the delivered gross samples of wood. Different fractions of the wood samples are highlighted to show that the samples are quite heterogeneous. For the FC experiments, only the spruce and birch wood was sieved into a fraction smaller and larger than 1 cm as shown in the figures. The GROT samples were used as received.

Figure 2.8 shows the Norwegian birch wood which contains considerable amounts of bark of substantial size. These bark pieces typically curl after drying. These large amounts of birch bark do not come as a surprise, as birch bark easily comes off its wood, whereas the spruce bark adheres
more tightly to the wood branches and chips. The birch bark pieces have a leathery feel and texture. The wood pieces smaller than 1 cm are finer and longer than the pieces that are larger than 1 cm. Their shape is rectangular and they have a maximum thickness of 0.5 cm.

![Gross Birch Sample](image)

Figure 2.8. Main constituents of the gross Norwegian birch wood sample.

Figure 2.9 shows the different fractions of spruce wood. There is bark present, but in smaller amounts (and in smaller pieces) compared to birch. The spruce bark is harder and looks more like wood, compared to birch bark. Overall, the spruce wood sample has a wider particle size distribution compared to the birch wood. The fraction smaller than 1 cm contains a fair amount of wood dust and the particles larger than 1 cm can be quite long. There is a fraction of flat pieces present, which are the hardest to carbonize, as will be discussed later.
Figure 2.9. Main constituents of the gross Norwegian spruce wood sample.

Figure 2.10. Main constituents of the gross Norwegian birch GROT wood sample.

Figure 2.11 shows the different fractions of birch GROT wood: twigs, branches with diameters of typically 1 to 2 cm and pieces of wood. There is bark present, but it is cut in such small pieces, that it is hard to identify them as bark.
Figure 2.11 shows the different fractions of spruce GROT wood. A large portion consists of needles, which much like bark have a high ash content of up to 4%. The higher ash content of the needles and bark will cause the overall ash content of the total sample to increase. Small branches with typical diameters of 1 to 2 cm are found and they usually have their bark still attached to them. Twigs with diameters of less than half a cm are also amply present. In the spruce GROT sample, light-colored wood pieces are found that look like shredding from cutting operations. These wood chips are expected to have the lowest ash content and during pyrolysis will behave much like true spruce wood. Loose bark pieces are not present in large amounts.

The spruce and birch wood was split up into a fraction that was larger and one that was smaller than one cm with a custom-made sieve (1 cm x 1 cm). Previous FC work has shown that carbonization of larger wood particles gives rise to higher fixed carbon yields [1]. At first it was not clear if the effect of particle size on Flash Carbonization performance was going to be the primary focus of this work (which will become a publication in Fall 2015), but the breakdown into small and large would do no harm. The spruce and birch GROT was used unchanged. This way the carbonization of the GROT would approximate a real life scenario, heterogeneity being the main difficulty in creating high quality charcoal from GROT.

Table 2.4 shows the higher ash contents of GROT relative to the non-residue wood itself. The ash content was analyzed in accordance with ASTM D1102, which requires to gradually heat up a wood sample (smaller than 40 mesh) up to 600°C several times in a row until it no longer loses
weight. A large GROT sample was ground below 40 mesh to ensure that a representative sample was being used. The ash content of different parts of Norwegian spruce varies between 0.18 to 2.11 %, dry basis (db) (ASTM D1102) and the various parts of the tree have different mineral phases, causing diverging behavior during melting/sintering [114].

<table>
<thead>
<tr>
<th>Type wood</th>
<th>MC</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%, wb</td>
<td>%, db</td>
</tr>
<tr>
<td>Spruce</td>
<td>10</td>
<td>0.37</td>
</tr>
<tr>
<td>Birch</td>
<td>9.2</td>
<td>0.34</td>
</tr>
<tr>
<td>Spruce GROT</td>
<td>9.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Birch GROT</td>
<td>9.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

When the FC canister was loaded, the canister was tapped with a rubber hammer or wooden block to remove any large air pockets from the wood bed.

Table 2.5 shows ultimate analyses performed by NTNU in Norway on the different wood samples. It shows that spruce and birch have very similar carbon contents while those of their respective GROTs are slightly higher. Both the spruce and birch GROT have elevated nitrogen (and in lesser amounts also sulfur) contents compared to the pure wood samples.

<table>
<thead>
<tr>
<th>Type Wood</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>%, db</td>
</tr>
<tr>
<td>Spruce</td>
<td>49.64</td>
</tr>
<tr>
<td>Spruce GROT</td>
<td>51.66</td>
</tr>
<tr>
<td>Birch</td>
<td>49.93</td>
</tr>
<tr>
<td>Birch GROT</td>
<td>50.74</td>
</tr>
</tbody>
</table>

*NA=Not Available.
Results

The results discussed in this section will feature in a future paper I will write together with Dr. Michael J. Antal Jr. in collaboration with NTNU in Norway. The charcoal and fixed carbon yield performance of the FC unit will be assessed, as well as the possibility of using Norwegian GROT or forest residues as a precursor to metallurgical charcoal. I will be using spruce and birch when I refer to ‘pure’ spruce and birch feeds. When referring to forest residues, spruce GROT or birch GROT will be used.

**Does thermal insulation of the reactor vessel have any benefits?** As explained in the FC Lab scale material section 2.2, a second canister was fabricated, identical to the original canister, but with a smaller diameter. The smaller diameter allows for the installation of extra Kao wool having superior thermal insulation characteristics.

The use of a better insulated FC canister has been inspired by experiments conducted on the demo-reactor, as discussed in section 2.3. The demo-reactor deploys a 0.46 m (18”) diameter canister (in a 0.91 m diameter FC vessel) capable of accommodating up to 55 kg of macadamia nut shells and corncob. There are larger canisters available, but as the canister itself grows in width (they all have the same length), we need more biomass for each run and more storage room for each batch of charcoal made.

All the experiments (see Table 2.6) done with a view to evaluating the effects of a smaller versus a larger canister, used Norwegian spruce smaller than 1 cm as a feed. The experiments done on February 12 and 19, 2015 had corncob loaded as tinder and as a sacrificial buffer layer on top because these two experiments were the first Norwegian wood carbonization trials to have been completed successfully.

Sam Wade [115] investigated deflagrations of corncob (which are the most vigorous) in the FC lab-scale unit and observed $\Delta P_{\text{max}}$ between 0.42 and 1.31 MPa with $\frac{dP}{dt}$ rates of 0.34-1.21 MPa/s. Small deflagrations have been observed for corncob and certain types of wood, but not for macadamia nut shells.

During the higher pressure experiments of 12 February and 9 April 2015 at 2.14 MPa, deflagrations occurred during the initial six minutes of heating. During the 12 February, 2015 experiment the pressure rose slowly from 2.17 MPa to 2.27 MPa whereupon it spiked to 2.47 MPa until the downdraft valve was opened to allow the gases to escape. The April 9, 2015 experiment showed multiple deflagrations within one minute, causing the pressure to first rise to 2.38 Mpa and then even to 2.49 MPa. These deflagrations are partly caused by temperature increases proceeding...
from the heater (we observed 650°C 7 cm above the heater, 600°C 15 cm above the heater and almost 400°C 30 cm above the heater at the time of the deflagrations) but equally well by the devolatilized gases from the biomass bed. The temperature profiles for the 12 February and 9 April 2015 experiments can be found in appendix D.

When using the smaller canister at 0.79 MPa, the fixed carbon content was higher than when the larger canister was used (83.5% compared to 80.2%). This tallies with the situation in the demo reactor which is also capable of producing extremely high fixed carbon content charcoals. It is probably worth examining whether filling the whole reactor vessel cavity with Kao wool (see Figure 2.3) could be effective in getting even higher fixed carbon contents. At 2.17 MPa, the difference in fixed carbon content is not as pronounced. The slightly longer 33 minute reaction time might have caused slightly higher devolatilization, resulting in lower VM contents. The charcoal and the fixed carbon yield drastically drop when the smaller (and better insulated) canister is used. A decrease of up to 5.5% has been observed.

By making the diameter of the canister smaller (permitting to load only a fraction of the biomass that could be loaded in the larger canister), there is more steel material compared to the amount of feed present in the experiment. For example, during the 19 February 2015 experiment, 6.1 kg of steel canister was present per kg of feed while during the 23 April, 2015 experiment, 10.3 kg of steel was present per kg of feed. This extra amount of steel might have influenced the carbonization process by retaining the heat from the combustion processes which should be used for pyrolysis.

Spruce wood (Picea Abies) has previously been carbonized in the $R^3$-Laboratory with a carbonizer [42] (named PDU) which was the precursor of the Flash Carbonization Lab reactor. At 1 MPa a fixed carbon yield of 28.8% was achieved while the theoretical fC yield is closer to 33%. Spruce wood is best carbonized at 2.17 Mpa (fixed carbon yield of 31.2%), because then it can reach 95% of its theoretical fixed carbon yield. The ash contents are not influenced by the canister used (and the change in heat migration), but seem rather dependent on the pressure in the system, which in turn influences heat transfer.
Table 2.6. Comparison between the two different FC canister sizes at low and high reactor pressure.

<table>
<thead>
<tr>
<th>Type</th>
<th>Size</th>
<th>Date</th>
<th>Reactor Pressure</th>
<th>Flow Rate</th>
<th>Reaction^a</th>
<th>Proximate^b</th>
<th>Charcoal Yield</th>
<th>fC Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Canister</td>
<td>Experiment yymmdd</td>
<td>MPa</td>
<td>psi/min</td>
<td>min</td>
<td>%, db</td>
<td>%, db</td>
<td>%, daf^c</td>
</tr>
<tr>
<td>Spruce</td>
<td>Large</td>
<td>150219</td>
<td>0.79</td>
<td>15</td>
<td>28</td>
<td>18.1</td>
<td>80.2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>150423</td>
<td>0.79</td>
<td>7</td>
<td>33</td>
<td>14.7</td>
<td>83.5</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Large</td>
<td>150212</td>
<td>2.17</td>
<td>15</td>
<td>31</td>
<td>18.8</td>
<td>80.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Small</td>
<td>150409</td>
<td>2.17</td>
<td>6</td>
<td>19</td>
<td>20.4</td>
<td>78.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

^aReaction time starts when the heater is turned on until the air supply is shut off.

^bProximate analysis done according to ASTM D1762-84.

^cAsh content found in Table 2.4 and measured with ASTM D1102.

Figure 2.12 shows the carbonized spruce wood and carbonized wood fragments (in Figure, right) that were glued to each other with a charcoal-like material that had the appearance of solidified tar.
Birch or spruce to make charcoal? Table 2.7 displays the experimental conditions and results of the FC process at 2.17 MPa for spruce, spruce GROT, birch and birch GROT. Despite the longer reaction time needed for GROT spruce and birch compared to the spruce and birch, the GROTs have reduced fixed carbon contents by almost 10%, and this also translates into higher volatile matter contents for the GROTs. The ash content of the GROT charcoals is a lot larger than the ash content of the spruce or birch wood charcoal, but this is merely because the GROT feed contains large amounts of ash to begin with. The fixed carbon contents of the birch GROT is a lot lower compared to the fixed carbon content of the birch wood, despite the longer reaction time of the GROT sample (the FC experiments 12 February 2015, 8 May 2015, and 13 May 2015 had similar mass loading, only 12 February 2015 had a lower amount of spruce loaded to allow for corncob tinder and a corncob sacrificial layer to be accommodated). When either spruce or birch wood is compared to their respective GROTs, a decrease in both charcoal and fixed carbon yield is observed. None of the charcoal yields are lower than 35%, but because of the lower fixed carbon contents of the GROT charcoal, the fixed carbon yield is low as well.
The GROT was loaded as received and was a mix of very small particles (needles in the case of spruce) and larger branches, while the spruce or birch wood loaded had a larger overall particle size. The effect of particle size has been investigated at elevated pressures (2.17 MPa) for oak wood. An increase in fixed carbon yield from 22.03% to 27.6% was observed [138]. On the other hand, the GROT ash content might have enhanced its fixed carbon yields as evidenced by previous work in the R3-Laboratory [16]. One should be reminded that the GROT is neither fine or coarse. It is a mixture that is similar to genuine forest residue waste that does not need any processing. From that point of view, the results for the GROT are promising.

Table 2.7. Comparison between the FC process performance of birch or spruce or their GROTs at 2.17 MPa.

<table>
<thead>
<tr>
<th>Type</th>
<th>Date</th>
<th>Flow Rate</th>
<th>Reaction</th>
<th>Feed Size</th>
<th>Proximate Analysis</th>
<th>Charcoal Yield</th>
<th>fC Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Experiment yymmdd</td>
<td>psi/min</td>
<td>min</td>
<td>cm</td>
<td>VM %, db</td>
<td>Ash %, db</td>
<td>%, daf</td>
</tr>
<tr>
<td>Spruce</td>
<td>150212</td>
<td>15</td>
<td>31</td>
<td>&gt;1cm</td>
<td>18.8 80.1 1.1</td>
<td>38.2</td>
<td>30.7</td>
</tr>
<tr>
<td>Spruce GROT</td>
<td>150512</td>
<td>12</td>
<td>52</td>
<td>AR</td>
<td>22.4 72.7 4.9</td>
<td>36.9</td>
<td>27.3</td>
</tr>
<tr>
<td>Birch</td>
<td>150508</td>
<td>14</td>
<td>39</td>
<td>&gt;1cm</td>
<td>21.5 77.6 0.8</td>
<td>40.0</td>
<td>31.1</td>
</tr>
<tr>
<td>Birch GROT</td>
<td>150513</td>
<td>12</td>
<td>47</td>
<td>AR</td>
<td>28.5 67.7 3.7</td>
<td>37.0</td>
<td>25.5</td>
</tr>
</tbody>
</table>

*a Reaction time starts when the heater is turned on until the air supply is shut off.
*b Proximate analysis done according to ASTM D1762-84.
*c Ash content found in Table 2.4 and measured with ASTM D1102.
*d AR=As Received.

Is there any benefit in carbonizing at higher pressures? The benefits of operating the FC reactor at higher pressures have been demonstrated in earlier publications [6] [1] [45]. Table 2.8 shows the difference between operating at 0.79 MPa and 2.17 MPa for spruce and birch. Spruce wood charcoal made at a pressure that is 2.7 times higher shows identical fixed carbon and volatile matter contents to the charcoal made at 0.79 MPa. The ash content is lower at higher pressure, which has been observed before. What differs is the charcoal yield, which is greatly enhanced (an increase of 6.5%) at higher pressures. Because the proximate analysis is identical and the charcoal yield increases, the charcoal made at 2.17 MPa also has a higher fixed carbon yield (31.2% versus 27.0%).

The birch wood (experiment done on 150702 in Table 2.8) was carbonized for an extended period of time, and as a result the full bed was completely carbonized (and significantly devolatilized). All other experiments had a very small fraction (40 g at the most) which was not completely carbonized but rather heavily torrefied. This fraction was removed and the charcoal yield was calculated using the equation 2.5. above. Because of the severe devolatilization a decrease in VM was observed,
which translated in a decrease of the charcoal yield (the charcoal yield in equation 2.4 can also be written as \( \frac{\text{mass of } fC + VM + Ash}{\text{mass feed}} \)). Due to the very low charcoal yield, the fixed carbon yield was low as well for the July 2 2015 experiment. The charcoal yield of the birch wood carbonized at 2.17 MPa was 40%, and because of the lower fixed carbon content, the fixed carbon yield was identical to the fixed carbon yield of the spruce wood.

Table 2.8. Comparison between a reactor pressure of 0.79 and 2.17 MPa for the carbonization of spruce and GROT.

<table>
<thead>
<tr>
<th>Type</th>
<th>Date</th>
<th>Pressure</th>
<th>Flow Rate</th>
<th>Reaction Time</th>
<th>Proximate ( b ) Analysis</th>
<th>Charcoal Yield ( fC ) Yield</th>
<th>Proximate Analysis ( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Experiment</td>
<td>yymmdd</td>
<td>MPa</td>
<td>psi/min</td>
<td>min</td>
<td>%, db</td>
<td>%, db</td>
</tr>
<tr>
<td>Spruce</td>
<td>150219</td>
<td>0.79</td>
<td>15</td>
<td>28</td>
<td>18.1</td>
<td>80.2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>150212</td>
<td>2.17</td>
<td>15</td>
<td>22</td>
<td>18.8</td>
<td>80.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Birch</td>
<td>150702</td>
<td>0.79</td>
<td>14</td>
<td>51</td>
<td>6.6</td>
<td>91.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>150508</td>
<td>2.17</td>
<td>14</td>
<td>39</td>
<td>21.5</td>
<td>77.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\( a \) Reaction time starts when the heater is turned on until the air supply is shut off.

\( b \) Proximate analysis done according to ASTM D1762-84.

\( c \) Ash content found in Table 2.4 and measured with ASTM D1102.

It is important to have a measurement of uncertainty and because the proximate analysis is done in triplicate, a standard deviation on the fixed carbon content can be calculated. The fixed carbon yield is a product of the charcoal yield and fixed carbon content on a feed dry ash free basis. The feed ash content is also done in triplicate. The average standard deviation of the fixed carbon yields for all the Norwegian wood FC experiments is 0.07%.

The benefits in terms of yields of operating at higher pressures are obvious. How does the production of charcoal at higher pressures translate into improved economic value for a ferrosilicon plant?

The following equation 2.15 estimates the cost to produce 100,000 metric tonnes of fC per year as a function of the harvesting cost of a tonne wood (\( \$ 100/\text{tonne} \) or \( \$ 0.100/\text{kg} \)) and the kg of dry wood harvested per year as in:

\[
\frac{\$}{\text{year}} = \frac{\text{kg dry wood}}{\text{year}} \times \frac{\$ 0.100}{\text{kg dry wood}} \tag{2.15}
\]

Where the kg of dry wood per year depends on the fC needs per year (100,000 metric tonnes of fC per year in our case), the charcoal yield (\( \frac{\text{kg char}}{\text{kg dry wood}} \)) and the fC content (\( \frac{\text{kg fC}}{\text{kg char}} \)) of the charcoal as shown in following equation 2.16.
\[
\frac{kg\, dry\, wood}{year} = \frac{100,000,000\, kg\, fC}{Yield\, (kg\, char/\, kg\, dry\, wood) \times fC\, content\, (kg\, fC/\, kg\, char)}
\] (2.16)

When combining equation 2.15 and 2.16, we are able to get an idea of the cost for a ferrosilicon plant in \(\$\) \(year\):

\[
\frac{\$\, year}{year} = \frac{100,000,000\, kg\, fC}{Yield\, (kg\, char/\, kg\, dry\, wood) \times fC\, content\, (kg\, fC/\, kg\, char)} \times \frac{\$\, 0.100}{kg\, dry\, wood}
\] (2.17)

Table 2.9 compares the benefits of operating at higher pressures by using the fC content and charcoal yields from FC experiment 12 and 19 February 2015 (which operated at 2.17 and 0.79 MPa, respectively), and inputs these in equation 2.17. Table 2.9 shows that by operating at 2.17 MPa, Elkem can save over 5 million \$ every year. Furthermore, Elkem prevents the harvest of 154 million kg trees (if we assume that freshly harvested wood contains 2 kg of water for every kg of dry wood). Note that this is 2.7\% of Norway’s annual tree fellings.

<table>
<thead>
<tr>
<th></th>
<th>0.79 MPa</th>
<th>2.17 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal Yield</td>
<td>33.5</td>
<td>39.0</td>
</tr>
<tr>
<td>fC content charcoal</td>
<td>80.2</td>
<td>80.1</td>
</tr>
<tr>
<td>$/year</td>
<td>$37,220,382</td>
<td>$32,011,268</td>
</tr>
</tbody>
</table>

The operation cost of a compressor that can handle 2.17 MPa is considerable and should be included in the calculation above. It has been calculated [18] that by operating at 2.17 MPa (instead of 1.27 MPa), the increased production (due to higher fC-yields) using higher pressures could possibly make the $120,000 for a compressor that can handle 2.17 MPa justifiable. The cost of a 1.27 MPa and 0.79 MPa compressor is $30,000 and $15,000 [116], respectively.
2.3 Demo-scale reactor

The flash carbonization demo-scale (short for demonstration scale) is the big brother of the lab-scale reactor that is discussed in detail in section 2.2. The demo-scale reactor was designed in the $R^3$-Laboratory and manufactured by McAbee Construction in 2002. It has a MAWP of 2.86 MPa (400 psig), compared to the lab-reactor’s 6.10 MPa (870 psig) MAWP. The working principles of the demo-reactor are very similar to the lab-scale reactor (the differences will be discussed below). They both consist of a FC vessel and FC canister, and they are both downdraft reactors with a heater at the bottom. The creation of a demo-scale reactor was a logical step for the further development and commercialization of the Flash Carbonization process as a whole.

Unlike the lab-scale reactor, no scientific papers have yet been published using the demo-scale reactor. Nonetheless, operating the demo-scale reactor (and successfully manufacturing charcoal without the creation of smoke) requires not only vast engineering knowledge, but also a step-by-step scientific approach and experimental design.

2.3.1 Apparatus

The 2015 demo-scale apparatus will be discussed below. Emphasis will be placed on the operation of the demo-scale reactor in synchronization with the retrofitted thermal oxidizer or afterburner. Some very peculiar differences between the demo- and lab-scale reactors will be explained; section 2.2 will be concluded with the results of our last four successful experiments.

Demo-scale vessel and canister

The demo-scale reactor is an enlarged version of the lab-scale reactor (0.91 m inner diameter and 2.83 m high (cylinder only) versus 0.15 m and 1.20 m for the lab-scale reactor). However, the demo-reactor is not a flanged pipe with two blind ends, but consists instead of a pipe section (made by McAbee by welding different cold-rolled pipe sections together) to which two elliptical heads are welded. This is economical to use because of the reduced wall thickness. The reactor volume of the lab-scale reactor (which resembles a cylinder) equals 0.021 m$^3$, while the volume of the demo-scale reactor is the volume of the cylinder plus two times the ellipsoidal heads ($\frac{\pi D^3}{24}$) where D is the inner diameter of the vessel. The inner volume of the demo-scale reactor equals 2.11 m$^3$, which is 100 times larger than the lab-scale reactor. The void volume of the piping connected to the FC reactor is not included in these calculations. The FC vessel itself is made of carbon steel. The top opens using a hinged, quick closure specially designed by McAbee Construction. The top lid is opened by means of a hydraulic ram and secured in place by a revolving ring (also operated by a hydraulic ram) that pushes the top lid against the vessel using an elastomer seal.
For the demo-scale reactor, three FC canisters of varying sizes are available. The largest fits tightly into the FC vessel and has an exterior diameter of 0.86 m (34"), while the other two have exterior diameters of 0.76 m (30") and 0.31 m (12"), and are centered using vanes attached to the side of the canisters. All canisters are made of carbon steel with schedule 20 and each is 2.74 m in length. During this research project, the 0.31 m diameter canister was primarily used. The lab-scale canister that is typically filled with biomass has a volume of 0.00895 m$^3$ (the canister with largest diameter) and 0.207 m$^3$ for the demo reactor (the 0.31 m diameter canister). If we assume identical mass loading (and particle void space), the ratio $\frac{\text{total volume}}{\text{canister volume}}$ for the demo reactor is more than four times that of the lab-scale reactor.

Compressed air is supplied to the FC vessel through 2.54 cm Swagelok lines by a gas powered Speedaire compressor with a maximum pressure of 1.31 MPa (175 psig), and a displacement of 0.24 m$^3$/s (27 CFM) at 0.72 MPa (90 psig). The flow rate of the compressed air to the FC vessel and canister is controlled by a large, 5.08 cm calibrated ball valve. As with the FC lab-reactor, the FC canister is connected to the compressed air supply by a flexible stainless steel tube.

The demo-scale reactor operates completely ‘off grid’. The power for the heaters, air blowers, electrical heating element (identical to the lab reactor, but spiral wound in a larger diameter) and the hydraulic pump (for opening and closing the top lid) is supplied by a Generac 17.5 kW generator. All other appliances, including the computer, labVIEW, pressure transducers and digital readouts are powered by a Honda EU2000i generator. A 550 VA APC battery pack can sustain the operation of the computer and labVIEW should the generator stop working.

During a typical FC demo-scale experiment, the temperatures inside and outside the FC vessel and afterburner are monitored and recorded via labVIEW, using the same NI SCXI-1000 unit as the lab-scale reactor. As the unit had become too unreliable and transporting this large piece of equipment is not easy, the demo-reactor was also coupled to the NI Compact-DAQ 9178 with the NI 9214 16-Channel Isothermal module. The temperatures of the FC vessel’s outer shell are monitored together with the temperature right below the vessel, where the effluent is allowed to flow to the afterburner. All temperature measurements are verified with a handheld IR thermometer. Dr. Manya (visiting professor specialized in carbonization systems from the University of Zaragoza, 2014) recommended that the thermocouple lines not be bent, as this could potentially distort the final signal. A new and enclosed cable was built to house all of the thermocouple lines. Pressures are monitored up- and downstream of the FC reactor vessel (the pressures of which deviate when air is supplied to the vessel because of an extra, dynamic pressure component) via analog gauges and digital Omega 5000 psig (34.6 MPa) PX602 transducers with their respective electronic readouts.
The afterburner has several thermocouples placed inside and outside the unit, and all thermocouples used are K-type.

A burst diaphragm which holds an Inconel Oseco rupture disc prevents the pressure in the FC vessel from rising above 1.54 MPa (209 psig).

**Thermal oxidizer**

The lab-scale effluent and its treatment are not discussed in section 2.2, as it was not part of this research project and because the POST building offers air gas cleaning through state of the art HEPA filters. The effluent from any carbonizer will be a mixture of CO, CO$_2$, hydrocarbons, particulate matter, N$_2$, O$_2$ (if too much air is supplied) and H$_2$O, and will typically be pitch-black in color. This effluent will usually possess enough carbon and energy to be combusted, which is no different than with the FC process. A catalytic oxidizer or afterburner was once coupled to the lab-scale reactor, the process development unit (the predecessor of the FC lab reactor [42]) had its effluent combusted by means of a flare.

The FC demo-reactor therefore definitely needs effluent treatment, as this is the only way to operate the carbonizer under the strict EPA and state emission regulations. As the demo-reactor is located in the middle of the University of Hawaii campus and adjacent to the Mid-Pacific Institute, the successful synchronization of the afterburner to the FC reactor is crucial.

In 2012, the demo-reactor was operated using a catalytic afterburner (with Condar steel monolith with platinum catalyst), which was ignited and preheated using propane. The catalytic afterburner consisted of several steel pipe units of different lengths, all 0.35 m (13.8”) in diameter and flanged together. Each tube was equipped with 5.08 cm (2”), 3.81 cm (1.5”) and 2.54 cm (1.0”) ports, both tangentially and perpendicular to the axis. The bottom tube was the tallest unit, 0.93 m in length, and functioned as a mixing chamber. The other, shorter pipe units were built to be modular and interchangeable with each other.

In 2013, the catalytic afterburner was converted to a thermal oxidizer/afterburner by installing refractory cement cassettes (with a temperature resistance of up to 1200°C) against the inside walls of one of the steel tubes. Several experiments were carried out in which the catalyst was heated to temperatures high enough to sinter off the catalyst and decrease the catalytic activity. The results were mixed, as the propane flow was forced in the side of the afterburner vessel and the force of the secondary air blowers together with the reactor effluent flow did not allow adequate mixing and long enough residence times to sustain a flame front in the afterburner.

In 2014, the thermal afterburner was rebuilt for a second time by casting a 2 cm layer of
refractory cement (using a Quikrete 10 concrete tube form) inside the afterburner vessel, as can be seen in figure 2.13. Former Hawaii State boiler inspector Matt Austin was a guide in designing this new thermal afterburner.

![Figure 2.13. Construction of the inner refractory cement layer in the thermal afterburner.](image)

On top of the mixing tube, a 2.4 m long sheet metal tube of the same diameter was installed to function as a stack. When the afterburner was designed and tested without the stack, the flames came out of the top of the mixing tube. Figure 2.14 shows a schematic of the thermal afterburner, together with all the used equipment to operate it.
Figure 2.14. Schematic of the TAB used to treat the effluent gases of the FC demo reactor. ACT: atmospheric condensates trap, VFA: valve forced air, VNAA: valve naturally aspirated air, DDV: downdraft valve, PT: propane tank, PV: propane valve, FRPV: flow regulating propane valve.
Figure 2.15 illustrates the side of the mixing chamber during operation. The vacuum blower is shown together with the calibrated VFA.

To preheat the thermal afterburner, sparkplugs are used to ignite a propane-air mixture. Throughout an FC experiment, the generated pyrolysis gases take over the role of the propane fuel, which then becomes the auxiliary fuel. Eventually the propane flow is discontinued in the run. These sparkplugs, which can be seen in Figure 2.14, are made of Swagelok and ceramic tube. The air that sustains this initial flame comes from a naturally aspired tube that can be opened or closed via a calibrated ball valve (VNAA in Figure 2.14). The propane flow is regulated by means of a needle valve (FRPV) and monitored with a Matheson Trigas FM1050 flow meter. With the press of a button, a Sunde 1.5 V battery powered igniter delivers a 12kV voltage to the sparkplugs, thereby igniting the propane-air mixture.

After a small propane flame is created, extra amounts of air are supplied to the afterburner via a vacuum blower the flow rate of which is restricted and regulated by a calibrated ball valve.
(VFA in Figure 2.14). The FC reactor effluent enters the afterburner from the bottom via a 5.08 cm diameter (2") T-section, the ends of which are pointed tangentially in the mixing tube.

Figure 2.16 shows the propane flame with the VFA at setting 2, with a moderate propane flow of 0.00038 $m^3/s$. Because the air is supplied tangentially, the flame becomes circular.

![Figure 2.16. Topview thermal afterburner without stack installed.](image)

The TAB exhaust CO measurements are taken with a CO Series 2500 from Blanke Industries Inc. This analyzer allows CO measurements of between 0-10% with a resolution of 0.01%. Blanke Industries promises a response time of less than 10 seconds. The CO sensor in the Blanke series 2500 has a lifetime of maximum five years, and should be calibrated regularly.

The TAB exhaust $O_2$ is measured by a TPI 709 combustion analyzer (which can also measure CO up to 1%). The oxygen can be measured up to 25.0% with an accuracy of 0.3%. The TPI 709 is equipped with a built-in water trap and particle filters that must be maintained on a regular basis. We also used a Bacharach Oxor III analyzer, which can detect oxygen up to 20.9% with an accuracy of 0.4%.
Differences compared to the lab-scale reactor

Both the demo and lab reactors work at a constant pressure, but the way in which this constant pressure is maintained varies between the lab- and demo-scale reactors. During a typical lab-scale experiment, one operator controls the downdraft valve (see DDV in figure 2.1), and one supplies air through the micrometer (MMV in figure 2.1) valve. The micrometer valve controller allows a specified flow of air into the FC vessel, while the goal of the downdraft valve operator is to maintain the pressure at a certain predetermined value throughout the experiment.

During a demo-scale reactor experiment, one of the main objectives is to create charcoal while eliminating smoke. Thus, the operator responsible for the afterburner will decide to what extent to open the DDV. The person controlling the air flow to the FC demo reactor must anticipate this and keep the pressure constant, never allowing the pressure to rise. A pressure rise could result in a runaway reaction.

During a lab-scale experiment, an accumulator is filled with air up to 20.8 MPa (or 3000 psig). For a demo-scale experiment, a gas powered compressor (with a small reservoir) is used, which must continuously pump air throughout the experiment. The speed at which the flame front moves upwards, and thus the speed at which an experiment takes place, is limited by the amount of air that can be supplied by the air compressor.

Before a demo-scale experiment can start, the propane tank is filled, and the compressor and generators are filled up with gas. The afterburner is allowed to heat up according to the start-up procedures I drafted, which can be found in appendix A. Figure 2.17 shows that the thermal afterburner in its current configuration needs approximately 30 minutes to heat up to temperatures (over 600°C for the TC 'TAB stack' and over 400°C for the TC 'TAB ignition') that can efficiently burn the reactor effluent. During this heat-up stage, 3.2 kg of propane is consumed.
2.3.2 Results

Four FC demo reactor experiments have been conducted with the new thermal oxidizer or afterburner in place, as shown in Table 2.10. Of these four, only the two most recent experiments were considered a success, as they were not attended by excessive smoke and succeeded in completely carbonizing the macadamia nut shell feed.

Table 2.10. FC demo reactor experiments using Macadamia nut shells with TAB to treat effluent.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Date</th>
<th>Mac Nut</th>
<th>Corncob</th>
<th>Fully Carbonized?</th>
<th>Proximate Analysis</th>
<th>Charcoal Yield</th>
<th>Fixed-Carbon Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>yymmdd</td>
<td>kg</td>
<td>kg</td>
<td></td>
<td>fC</td>
<td>VM</td>
<td>Ash</td>
</tr>
<tr>
<td>150414</td>
<td>49</td>
<td>11</td>
<td></td>
<td>Yes</td>
<td>96.9</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>150304</td>
<td>51</td>
<td>11</td>
<td></td>
<td>Yes</td>
<td>97.0</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>150127</td>
<td>53</td>
<td>14</td>
<td></td>
<td>No</td>
<td>97.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>141229</td>
<td>50</td>
<td>17</td>
<td></td>
<td>No</td>
<td>95.6</td>
<td>2.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Table 2.10 shows the proximate analyses results for the macadamia nut shell charcoal. It had a fixed carbon content over 95%, but because of the low charcoal yields, its overall fixed carbon yield is slightly above 21%. The FC lab-scale reactor could reach fixed carbon yields of 34% (with a fixed carbon content of 93%). The average standard deviation of the fixed carbon yields for all the Macadamia nutshell FC demo reactor experiments is 0.14%.

In the metallurgy and the silicon industry fixed carbon is one of the most important ingredients, since it is the fixed carbon that reduces iron oxides or silicon dioxide into iron ore or silicon to produce metal and silicon wafers. Since 1830 smelters like Hickam, Williams and Company have been selling metallurgical cokes that have fC contents of up to 92%, VM of up to 1% and ash contents of 7%. The macadamia nut charcoal produced using the FC demo reactor easily reaches fC contents similar to calcined petroleum cokes (99%).

The advantage of the FC lab reactor is that the FC process produces metallurgical cokes in one straight batch using the heat of its own process while most industrial processes first make charcoal (or buy coal) and then devolatilize the coal or charcoal by burning expensive petroleum as a heat source. If our target market requires charcoal with fC contents at round 80% (and not +95%), the operators of the demo reactor could increase the charcoal yield by running shorter at the same flow rate, or running the same time (or longer) at a lower flow rate. By running shorter, the bottom charcoal will be less devolatilized and the upper charcoal in the canister might only be partly carbonized. These could be carbonized in the next FC experiment.

This idea of running shorter might bring the ‘flash’ back to Flash Carbonization. What’s more, charcoal with a very high fC content is fragile compared to other lower fC charcoal (while the metallurgical industry needs reductants with considerable strength, as the cokes bed may collapse).

A road of trial and error
The operation of the FC demo scale reactor requires a considerable amount of teamwork and the synchronization of the engineers’ work. Both the two generators and the compressor are pretty noisy, making verbal communication impossible.

The operation of the demo reactor has become a lot more clear recently, as I was allowed to buy 3M Peltor PowerCom wireless headsets which combine hearing protection and 2-way communication. Questions can now easily be asked and urgent matters can be communicated in a swift way.

The first two demo reactor runs (27 January 2015 and 29 December 2014) in Table 2.10 were not successful, as the afterburner did not sustain its operation and the macadamia nut shell bed did not completely carbonize. An overview of the 27 January 2015 experiment can be found in
appendix E. The afterburner had a flame-out for too long, but was able to restart and continue running throughout the experiment. The experiment was halted too soon, as part of the bed was still uncarbonized. The FC demo reactor experiment done on March 4, 2015 had a similar (but more severe) afterburner flame-out, but the macadamia nut shell bed was completely carbonized!

From previous experiments we learned that, with the primary air valve fully opened, a 60 minute full air flow was needed for carbonizing a macadamia nut shell bed. To facilitate things, a list was drawn up and made accessible to all, based on pressure and temperature graphs from previous experiments (see appendix E), of significant events in the carbonization process that could be used as an indication as to when to stop the process.

- Pressure fluctuations
- Decrease in TAB temperatures
- Temperature FC reactor shell Bottom-Mid ≥ Top-Mid
- Rising CO/O₂ concentrations
- No noticeable flame in TAB, but high temperatures

Before conducting a next FC demo reactor experiment, a cold flow test was done to determine if the TAB flame was either disrupted by the moisture of the macadamia nut shell bed or by the volumetric flow of air inside the reactor. This cold flow test (done on April 10, 2015) was important as it would provide an answer to one of the questions we had during the March 4, 2015 experiment, viz. the occurrence of flame-outs when the downdraft valve is opened. Is it because a large amount of air is released into the TAB or is it rather the water content of the feed that disturbs the flame? If the TAB experiences a flame-out because too much compressed air is being fed to it, the operator should decrease the secondary air flow for a moment. If the moisture is the cause of the flame-out, the operator should be aware of the necessity to create a stronger flame by increasing both the propane and secondary air flow.

The results of this cold flow test were surprising: with the secondary air flow at 1 and the propane at 3/8 of a turn, we could not extinguish the flame with compressed air with the downdraft valve open at setting 2 (The downdraft valve has 6 spokes on its hand wheel, which are numbered. We usually never go beyond setting 2 on the downdraft valve during an experiment). Instead it made the flame more intense and pushed the flame upwards into the TAB.
The 14 April 2015 experiment was a great success. The afterburner had a small flame-out, but was re-ignited very swiftly. The list of signs that tell us when the carbonization reaction had come to an end was condensed and refined to:

- Decrease in both TAB temperatures
- Rising CO/O\textsubscript{2} concentrations, when other settings in the TAB stay the same
- No noticeable flame in TAB

Figure 2.18 shows 3 consecutive flame-outs between 10 and 23 minutes, where the CO concentrations increased (this region is highlighted with a grey dashed box. From 80 minutes onwards, CO and O\textsubscript{2} levels seemed to be increasing together with dropping temperatures in the afterburner.

![Figure 2.18. Overview of the temperature and CO/O\textsubscript{2} readings during the FC demo experiment done on April 14, 2015.](image)

Similar to the WHTB work discussed in a later section, there was some concern regarding the accuracy of moisture content measurements. When unloading the FC demo reactor canister, there is a time lag between weight measurements and moisture content analyses (which are typically done in the R\textsuperscript{3}-Laboratory). The unloading and weighing of the charcoal takes up to 30 minutes, and for the careful separation of the macadamia nut charcoal and corncob charcoal, an additional 30 minutes might be needed. During this 30 minute period, multiple samples of the macadamia nut and corncob charcoal were taken and isolated in airtight Ziploc bags. These samples were later analyzed.
on their moisture content. It was found that the moisture content of mac nut charcoal increases from 1.3% to 1.5% between the first and last weighing. The moisture content of the corncob charcoal changes from 1.4 to 2.6%. When the macadamia nut charcoal was subjected to proximate analysis in the $R^3$-Laboratory, the moisture content was 4.1%. These differences in moisture content will propagate into the charcoal and fixed carbon yields, which are of paramount importance. To avoid these discrepancies in moisture content measurements, right after unloading the charcoal, a charcoal sample is put in an airtight ziploc bag (to retain its MC). We have determined the signs that tell us when it is appropriate to stop the FC experiment, so that a skillful operator is able to keep the afterburner running well. Next steps are to decrease the amount of propane used (we went from 40 minutes of propane flow on 29 December 2014 to less than 28 minutes on 14 April 2015), to stop the experiments a little bit sooner in order to have a less devolatilized charcoal, and to solve the flame-out issue, as discussed in next section.

**Solution to afterburner flame-outs**

The 14 April 2015 demo reactor experiment was successful, but still almost three flame-outs occurred. So, in order to improve the afterburner’s user-friendliness, a new design for the downdraft valve has been suggested, as this valve opens too much (even when the operator only slightly turns the hand wheel).

The compressed air leaves the compressor through a 1.27 cm (0.5”) opening and gets delivered to the FC vessel by 1 or 2 lines. This orifice has a surface area of 1.27 cm$^2$. If the FC reactor is not in operation, as soon as the downdraft valve opening reaches 1.27 cm$^2$, the system is in steady state. As from that moment, the degree of opening of the downdraft valve no longer matters, as the flow of air coming out of the FC vessel will remain the same. This is an indication of how little control this large valve has in delivering small amounts of air to the afterburner.

The downdraft valve disc is 3.81 cm (1.5”) in diameter and to open the downdraft valve to 1.27 cm$^2$, we need to lift the plug of the valve so much, that the surface area of the compressor orifice becomes as large as the area of the downdraft valve opening.

$$2 \times \pi \times R \times H = 1.27cm^2 \quad (2.18)$$

With $R=\frac{3.81\text{ cm}}{2}$ we get $H = 0.11$ cm, which is the height the valve disc can travel before it creates an opening with the same area as the orifice of the compressor. The Bonney forge HL-31 5.08 cm (2”) diameter downdraft valve measures 0.42 cm per thread or revolution (6 threads per inch). The valve hand wheel has 6 spokes (with each spoke assigned a number by way of calibration). So the
valve disc moves up 0.42/6 or 0.07 cm per spoke. The rotations the hand wheel can make until we reach the point after which further opening of the valve is useless, are as follows:

\[ V\text{alve hand wheel spokes}_{\text{no control}} = \frac{H}{\text{cm/rotation}} = \frac{0.11 \text{ cm}}{0.07 \text{cm/rotation}} \approx 1.5 \quad (2.19) \]

After rotating the hand wheel one and a half spoke (or setting 1.5), further opening will not increase the flow out of the canister, when the system is at steady state. During operation the biomass feed will devolatilize and create more gases. This will change the number of rotations we can make. This example shows that the installed downdraft globe valve cannot control the air flow out of the FC reactor as accurately as we would like to.

Under supervision of Matt Austin (former State of Hawaii Boiler inspector), I designed a new valve disc that would allow minimal changes of exhaust flow while being safe (in such a way that, if the FC reactor has to be depressurized fast, the valve disc also permits large flows). Figure 2.19 shows the original valve disc on the left (A) and the new proposed design (B) on the right. The new valve disc does not simply rest on the valve seat. Instead, it goes partly into the valve seat hole (with 0.02 mm clearance) and allows flow through thin slots on the side of the valve. Instead of the exhaust passing next to the valve disc, the exhaust passes through the new valve disc and escapes through the slots, which become larger if the hand wheel is turned more. The new design allows a smaller area change per rotation of the hand wheel.

The slots have a surface area of 0.6 cm\(^2\), so to get the same area as the orifice of the compressor, we need \(\approx 2\) slots. As only part of the slots will be uncovered during operation, the valve control will be optimal. More slots will be made, as gases will be generated during the demo scale flash.
carbonization operation. First the valve will be analyzed during a cold flow test. Figure 2.20 shows the newly built valve disc using lathes and drill presses. The new valve disc is attached to the valve stem by means of a base plate and screws. The original valve disc was attached to the stem by means of a weld rod.

![Figure 2.20](image_url)

Figure 2.20. Overview of the newly created valve disc for the demo-reactor down draft globe valve. A: Bonney forge 2" 800 class valve with its original valve disc taken from the valve stem. B: Newly manufactured valve disc with 2 sloths (left) next to the original valve disc (right). The new valve disc can be removed quickly (instead of being welded on). C: top view of the new hollow valve disc.

Additional computer generated drawings which were a guide during the construction of the new valve disc are included in appendix F. The new valve disc has to be tested before it is put to actual use but that is beyond the scope of this work.
CHAPTER 3
WALL HEATED TUBING BOMB CARBONIZATION

3.1 Introduction

Cellulose \((C_6H_{10}O_5)_n\) is the most common organic polymer present on this planet, accounting for up to 50% of total biomass [117], and the earliest traces of its use date back to ropes made out of hemp found in China dating 4,500 BC [118]. After its identification by the French chemist Anselme Payen in 1838 [119], cellulose quickly became a focus of pyrolysis aficionados, bent on modelling or understanding the pyrolysis of cellulose, and subsequently extrapolating this knowledge to wood or other ligno-cellulosic materials like corn stover, sawdust or Elephant grass to name but a few.

Cellulose in lignocellulosic biomass forms a skeleton that is surrounded by hemicellulose, functioning as a matrix, and encapsulated by lignin [120].

Despite the fact that cellulose has been under investigation for over 150 years, there is still a lot of disagreement [121] concerning the exact kinetics of cellulose pyrolysis. Many models have been developed that try to explain the kinetic behavior and mechanism of cellulose decomposition during pyrolysis [122] [123]. Moreover, the operation of thermogravimetric analyzers, used in kinetic studies, may seem easily done at first sight, but it is obvious that it requires very skillful researchers to obtain reproducible results [124].

The pyrolysis of cellulose is not a one-step process. It is in fact composed of thousands of elementary reactions [125] and many a researcher observed the occurrence of an intermediate state during pyrolysis, assuming the appearance of a liquid or a very viscous substance, depending on the conditions. They actually perceived it through high speed photography [126]) and named it active cellulose, molten cellulose - because of its resemblance with the cellulose actually being molten, although the intermediate state shows a different composition than cellulose itself. Depending on the process conditions, this intermediate phase features varying chemical and physical characteristics. Typically, the formation of this intermediate phase is observed between 245°C and 477°C and the reducing ends [127] will decompose first.

Phase change phenomena, which do give the impression that the cellulose is actually melting, have also been observed in lignin, hemicellulose, wood, coal and certain plastics when exposed to elevated temperatures. Cellulose has been liquefied, without being decomposed, into a transparent solid by laser irradiation while supplying pressure and sheer force [128]. During pyrolysis, one of the products generated is levoglucosan (1,6 - anhydro - \(\beta\) - D - glucopyranose), but also celllobiosan and anhydro oligasaccharides which can, depending on the conditions, either evaporate [129] or
Whether levoglucosan originates from cellulose directly, or through secondary reactions is in dispute [130]. The polymerized levoglucosan is able to dehydrate to char [131], a process which is enhanced by elevated temperatures and pressures.

From the beginning of cellulose research in the early 20th century, vacuum pyrolysis of cellulose produced high liquid yields of 76% (and low char yields of 10%). For almost a century, the focus was predominantly on liquid production from cellulose [121]. Today levoglucosan (which can cost $79 for one g [132]) is the preferred product because it is thought to have biofuel qualities [133]. It is surprising that some of this bio-oil research has been funded by oil companies. Atmospheric and especially vacuum conditions favor levoglucosan yields while larger samples create more char [131]. The higher char yields when bigger samples are used was also observed by Wang et al [1]. Shoji et al [134] describe film-like charcoals made out of micro-crystalline cellulose heated to over 500°C in a constant N₂ flow. They had an average charcoal yield of 5% and no proximate analyses were available as this was not the main point of interest of the researchers.

The intermediate liquid can undergo secondary decomposition into char, which can also function as a catalyst itself because of its alkali metals [135]. Under atmospheric conditions, char yields of 10.9% were obtained using several TGAs [124]. Unfortunately no fC yields were calculated. Antal and Mok [136] obtained cellulose charcoal yields of 22% at pressures of 2.5 MPa in sealed vessels. In another research project of Richard and Antal, 41% yields at 2 MPa were obtained from cellulose [137]. They did not observe any liquid phase [4]. Figure 3.1 combines the results from two papers by Mok et Antal [4] [5] and shows how the charcoal yield of cellulose is maximized at low flow rates and high pressures, which are the conditions at which the overall reaction becomes exothermic. It is exactly this exothermicity caused by secondary reactions that lowers the heat needed and increases the char yields [138]. Generated tarry vapors, such as levoglucosan, have smaller specific volumes at increased pressures, increasing their time to decompose to secondary char [122]. Reaction rates increase because of increased concentrations. In addition to this, low flow rates enhance these two phenomena.
Figure 3.1. Effects of pressure and gas flow on the char yield and exothermicity of the pyrolysis reaction Source: [4] [5].
In a previous publication that I co-authored (see appendix C), we evidenced that pressure carbonization of cellulose in constant volume vessels or WHTB is capable of producing high fixed carbon yield charcoals which seem to have gone through a liquid phase during pyrolysis. When the pressure in the reactor exceeds the vapor pressure of the intermediate liquid, no boiling occurs, and condensation reactions in the liquid phase give rise to high fixed carbon yield charcoals. The exact composition of this intermediate liquid is unknown and the exact pressure needed is not known either, but during flash carbonization, the increase in charcoal and fixed carbon yields can be attributed, again, to the smaller specific volume of the produced vapors [16]. So even if we do not exceed the vapor pressure, charcoal formation is favored.

Certain conditions have to be met if we want to create high quality charcoal (i.e. high fC yield) out of cellulose. Too low pressures and high flow rates (0.5 MPa, steam flow) lead to average cellulose charcoal yields below 20% (and no molten phase) as observed by Ragucci et al [139]. Cellulose moisture contents can affect quantity (36.5 to 40%) and quality charcoal as evidenced by Mok et al [136].

The pyrolysis in sealed vessels is very promising because if the conditions that favour enhanced charcoal and fixed carbon yields are understood, it will be possible to extrapolate this data for cellulose to other lignocellulosic substances. The observation of these high yield liquid phase charcoals will influence how we will build reactors in the future. This will be discussed in section 3.4. This chapter reviews the effects of reactor pressure, HTT and moisture content of the cellulose feed on the characteristics and performance of the carbonization process in closed WHTB vessels.

3.2 Apparatus and experimental procedures

Following the successful results of the wall-heated tubing bomb experiments in our previous work [140], further progress has been made on Avicel cellulose carbonization experiments using upgraded apparatus under changed experimental conditions.

The preceding paper [116] was a preliminary study which explored the idea of creating high quality molten chars from cellulose under different pressurized gases. The present work builds on previous experiments using upgraded apparatus and a fully integral tubing bomb system. It elaborates on our earlier work involving experiments with varying sand bath temperatures, tubing bomb pressures, Avicel cellulose moisture contents, constant pressure and constant volume conditions, and the use of pressurized \(N_2\) as an initial gas. The apparatus and experimental procedures section will to some extent be similar, but considerably diversified compared to our previous work.
3.2.1 Apparatus

The experiments involve the use of a tubing bomb reactor which is plunged into a fluidized sand bath. Before an experiment is started, the sand bath is preheated and brought up to the desired temperature. The Wall-Heated Tubing Bomb apparatus (WHTB) is then loaded with microcrystalline cellulose, pressurized to elevated pressures from slightly above atmospheric to 4.8 MPa (680 psig) and lowered into the preheated sand bath. The WHTB is capable of making a high quality solid piece of char, which shows evidence of a molten phase, out of the packed cellulose feed. Note the use of "char" instead of "charcoal", as will later become clear, the VM contents are too high to call our solid product a charcoal.

Figure 3.3 shows a close-up of the WHTB, while Figure 3.4 shows the Wall-Heated Tubing Bomb System (WHTBS) as a whole. As the legend in Figure 3.3 indicates, the parts shaded in red are heated by the sand bath, while the blue sections are parts that are not (directly) heated. Light yellow shading shows the location of the cellulose feed. Kao and glass wool are placed, in this order, on top of the cellulose, to prevent cellulose from being blown up into the upper lines when the WHTB apparatus is pressurized. Figure 3.2 shows the glass wool on top of the kao wool after an experiment.

Figure 3.2. Glasswool on top of Kao wool.
Kao wool is used in closest proximity to the cellulose because it shows superior qualities compared to the glass wool. It does not entrap the char as much as the glass wool, and it has an extremely high temperature resistance of up to 1300°C.

Figure 3.3. WHTB apparatus with heated parts in red and cooler parts in blue.

The axis thermocouple measures the temperature inside the cellulose bed and is centered by a perforated thermocouple holder, which is in turn centered in the apparatus by means of a spider.
The entire setup is fabricated out of 316 stainless steel (SS) Swagelok fittings, and the WHTB apparatus unit uses a 2.54 cm (1”) outer diameter Swagelok tube with a wall thickness of 0.21 cm (0.083”) (rated 21.5 MPa (3100 psig) at 37°C, (down) rated 18.3MPa (2635 psig) at 300°C using ASTM A269). The WHTB apparatus is connected to its upper, colder sections using 0.635cm (1/4”) SS Swagelok lines (rated at 35.3 MPa (5100 psig) at 37°C). The upper line construction accommodates three Swagelok needle valves rated at 41.5 MPa (6000 psig) at 37°C. Two of those valves are used to pressurize or depressurize the reactor during loading and unloading, and are marked as V3 and V4 in Figures 3.3 and 3.4.
Using a third valve, V5, a burst diaphragm and pressure sensor can be disengaged in the event that vacuum is employed. The V5 valve makes this section multifunctional: when the valve is open, this section is used for safety purposes; when the valve is closed, vacuum can be deployed. The valve makes it possible to store part of the pressurized gases during void volume measurements. The diaphragm holder is rated at 20.8 MPa (3000 psig), and the diaphragm itself at 15.5 MPa (2235 psig) at 20°C. The diaphragm itself has a burst tolerance of 5%, and at 100°C the pressure allowed ranges from 13.6 to 15.0 MPa (1953-2157 psig). The Omega-brand thin film pressure sensor (PX 602-5KGV, rated at 34.6 MPa (5000 psig)) is used in conjunction with a DP25-S Omega digital readout. The type K thermocouples, also supplied by Omega, measure temperatures at different locations: four outside and one on the axis in the center of the WHTB.

Figure 3.3 and Figure 3.4 show the nomenclature of the volumes used in this work. The WHTB total volume consists of \( V_{bomb} \), which has an empty volume of approximately 0.1 L, and the sequestered volume \( V_{SV} \), which has a typical volume of 0.025 L. Before (with cellulose inside) and after (with cellulose char inside) each experiment, the volumes of the different WHTB sections are measured. The initial volume of the gas in the reactor is \( V_{bomb} \) and \( V_{SV} \) as shown in Figure 3.3 and Figure 3.4. The bomb volume includes the void volume \( V_{void} \), the active dead volume \( V_{ADV} \) and the dead volume \( V_{DV} \). We have assumed that \( V_{DV} \) and \( V_{SV} \) do not take part in the reactions (and are thus called inert volume \( V_I \)), although they might transfer water vapor, while the sum of the \( V_{void} \) and \( V_{ADV} \) will participate in the pyrolysis process proper and is called the active volume \( V_A \).

Each volume section in Figure 3.3 is calibrated by pressurizing certain sections using a calibrated air cart \( V_{cart} \) of 0.6 L. Subsequently, the air is used to displace water out of the polycarbonate water displacement vessel (WDV), which is weighed and converted to volume. Figure 3.5 shows the water displacement vessel that was custom-made in the \( R^3 \)-Laboratory. The upper vessel is used to fill the bottom vessel via Swagelok lines. A three-way valve allows easy operation.
Because of the extreme environment (high temperature and pressure together with abrasive sand), the heated part of the WHTB apparatus must be replaced after approximately 10 experiments. New volume ($V_A$) measurements of this (identical) piece of equipment are carried out by filling it with water, weighing it and converting it to volume. The active volume has an average value of 0.066 L.

3.2.2 Experimental procedure

Microcrystalline cellulose (FMC Biopolymers type Avicel PH102NF Lot P213826318) is used in these experiments and its properties are summarized in Table 3.1. The cellulose is subjected to elemental analysis and a higher heating value (HHV) analysis by Huffman Hazen Laboratories, a Division of Hazen Research. The ash analysis has been provided by FMC Biopolymers and confirmed at the University of Hawaii using ASTM D3516-89. Figure 3.6 shows how much cellulose (left) is needed to yield a small amount of ash (right).
The cellulose typically has a moisture content of 5%, wb, as measured at the UH; before every experiment it is analyzed according to a cellulose-specific ASTM 1348-94 in a Lindberg/Blue convection oven at 105°C using glass weighing bottles, which are closed with a stopper during handling for accurate measurements. A specific amount of cellulose is loaded into the annular region of the tubing bomb. In order to accurately measure the mass of cellulose, different weighing calculation modes are used to account for errors. During loading, the Swagelok tube is tapped to allow the cellulose to settle well and to eliminate any air pockets. The tube is filled with cellulose, while space is left to place first the Kao wool and then the glass wool. The initial volume available in the apparatus \( V_{\text{bomb}} \) is found using the Ideal Gas Law by repeatedly pressurizing the apparatus up to five times with air from a calibrated air cart, while recording the pressure in both the air cart and the WHTB apparatus.

To purge the vessel with a gas prior to an experiment, the apparatus is pressurized at least three times up to the desired initial gas pressure (e.g. \( N_2 \) or \( CO_2 \)), and then depressurized.

The WHTB apparatus is partly submerged in a Techne Fluidized Sand Bath Model SBL-2D (see red-shaded area in Figure 3.3) by lowering it with a small electric hoist. The thermal capacity of the alundum sand facilitates fast heat-up from room temperature to 300°C. In addition to its appreciable heat transference characteristics, the sand bath also has a uniform temperature throughout the whole process.

To terminate the experiment, the WHTB reactor is lifted out of the sand bath and cooled using an electric fan to room temperature. Depending on the type of experiment, it is terminated as follows: experiments done at a constant 300°C (or lower) sand bath temperature are halted.
10 minutes after an exotherm is observed, experiments done with an increasing temperature between 300 and 400°C are terminated when 400°C is reached. Data are collected with a National Instruments SXCI 1303 module which uses LabVIEW to condition and record temperatures (with a sample time of one second) inside the apparatus (TC axis) and the outer walls and the pressure inside the tubing bomb. Excel is used to further analyze all collected data.

Safety is key and the experiments with the tubing bomb are conducted in an enclosed structure made of Unistrut beams and protected with Lexan sheets, as can be seen in Figure 3.7.

![Figure 3.7. Structure made to cover the WHTB during experiments.](image)

### 3.2.3 Pyrolysis gases

For the purposes of analyzing the pyrolysis gases, the WHTB is depressurized into a custom-made 7 L polycarbonate water displacement vessel (WDV). Via a quickconnect J2 and valve V4, the WHTB is connected to the WDV and O1 is opened. A Swagelok bellows-sealed metering valve, V10, then allows us to carefully seep the gas into the WDV. The amount of water pushed out of the
WDV is weighed, which allows the measurement of $V_{WDV}$. Using the Ideal Gas Law, the resulting $V_{bomb} + V_{SV}$ can be calculated [140].

The gases are sampled with a needle equipped with a water trap in the Tygon tubing (inline 2x glass wool filter and Drierite) that leads to a 490 micro GC (Agilent Technologies). The GC has two columns installed, both of which use ultra-high purity helium carrier gas with 80 ms injection times for both columns together. Helium is connected to the GC via a Restek Oxygen and Moisture trap. Ne, $H_2$, $O_2$, $N_2$, $CH_4$ and CO are analyzed using a 10m Molsieve 5A with a back flush of 11s, pressure of 30psi and column temperature at 80°C while CO2 is analyzed with a 10m PolarPlotU column with a 17s back flush, a 17 psi pressure and column temperature of 60°C.

The GC is calibrated before every WHTB experiment using Matheson Micro MAT 105 mixtures GMT 10406TG and GMT 10403TG for CO2, CO, $O_2$, $CH_4$, $H_2$ and $N_2$ gases. Vacuumed 1 L Supelco inert foil gas sampling bags are used to transfer gases. Air is used as a calibration gas for Ne. Maider Legarra is responsible for the gas analyses.

### 3.2.4 Pyrolysis solids or chars

After the tubing bomb gases have been transferred to the WDV, the char is removed in a sequential order that is similar to the order used while loading the cellulose, but in reverse. The weighing method applied while loading the tubing bomb will be amply documented in the Master thesis by Charissa Higashi, who also worked in the $R^3$-Laboratory in 2014/2015. The Kao/glass wool is subjected to a moisture content analysis according to ASTM 1576-13 at 105°C in a convection oven using 57 mm aluminum dishes.

The char moisture content is analyzed with ASTM 1756-08 in a vacuum oven using 107 mm aluminum dishes. In order to forestall possible errors by analyzing samples with a limited amount of char, a total moisture content analysis is performed on the entirety of the char product. The moisture content analysis prior to the proximate analysis might seem redundant, but from experience we know that during handling and grinding for the proximate analysis, a large amount of moisture evaporates. Therefore the moisture content values yielded by the proximate analysis are not reliable, and are useful only for characterizing sub-samples on a dry basis.

After the moisture content analyses are completed, the char is ground using a mortar and pestle below 20 mesh. A mill is not used to grind samples because of the limited amount of char sample from each experiment. It is then loaded into 35x29mm porcelain crucibles that are subjected to a proximate analysis according to ASTM D1752-84, using an Isotemp vacuum type 282A oven at 105°C and 0.015 MPa for the moisture content analysis and a Thermo Scientific 1400 Thermolyne
furnace at 950°C or 750°C for the volatile matter and ash content analysis. All values are given on an oven dry basis, except for the moisture content values, which are on a wet basis.

3.2.5 Carbon mass balances

Each WHTB experiment is concluded by creating mass balances over the whole process (for example Tables 3.15 and 3.16 conclude with detailed mass balances of each WHTB experiment at the bottom). No experiment is perfect, and during every WHTB experiment there is an 'unknown component' or error, as we can rarely recover the exact amount of mass loaded. This unknown mass could be water, pyrolysis gases or char lost when the reactor is unloaded.

The following schematic (Figure 3.8) shows a typical mass balance for a WHTB experiment. The (wet) cellulose at the beginning of the experiment will decompose and recombine into char, gases, water and an unknown. The water recovered at the end originates from the initial water in the cellulose (cellulose at $R^2$-Laboratory conditions has an MC of approximately 5%, wb, hence the designation 'wet') and the water vapor released during the pyrolysis reaction.

![Figure 3.8. Schematic of a typical WHTB cellulose mass balance.](image-url)
These mass balances are important to our experiments, but there is a better way to measure the recovery performance of our WHTB trials: the carbon mass balance or carbon balance (CB). The C, H, O composition of the VM and the fC content, together with the amount of CO and CO$_2$ carbon gases, are used to calculate carbon balances for the WHTB cellulose experiments to be published in a future paper. The CB can tell us if a flawed MC analysis introduced severe systematic errors into our fC yield values, if a valve was not closed and gases were lost, or if an operator did not recover all the char made.

To obtain a char sample sufficient to allow Huffman Hazen Laboratories to perform reproducible C, H, O or ultimate (in accordance with ASTM D 3176 and D5373, ash analysis done at 750°C for 8 h) and Higher Heating Value (HHV) (in accordance with ASTM D5865) analyses (see Table 3.1), the WHTB experiment at an initial N$_2$ pressure of 4.79 MPa and at a constant sand bath temperature of 300°C was reproduced six times. Huffman Hazen Laboratories executed ultimate and HHV analysis on the cellulose char sample (designated Avicel cellulose char), and on the same char sample, devolatilized according to the volatile matter step in the proximate analysis ASTM D1752-84 (designated Avicel cellulose carbon). This latter can also be called a carbonized char [141].

The carbon (C) content in the VM is calculated as shown below (assuming there is no ash present):

$$%C \text{ in } VM = 100 \times \frac{\%C \text{ Char } 350}{100} - \frac{\%C \text{ Char } 950}{100} \times \frac{1 - \text{ VM} \%}{100} \quad (3.1)$$

The VM% in equation 3.1 is 41.9% which is calculated by devolatilizing the Char 350 (see Table 3.1).
Table 3.1. Avicel cellulose feed and char characteristics.

<table>
<thead>
<tr>
<th></th>
<th>MC [% wb(^a)]</th>
<th>Elemental analysis [% db(^b)]</th>
<th>HHV(^c) [MJ/kg]</th>
<th>Ash(^d) [% db]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>Avicel Feed</td>
<td>4.33</td>
<td>44.57</td>
<td>5.98</td>
<td>49.75</td>
</tr>
<tr>
<td>Avicel Char,350(^\circ)C</td>
<td>13.97</td>
<td>74.82</td>
<td>2.99</td>
<td>20.68</td>
</tr>
<tr>
<td>Avicel Carbon,950(^\circ)C</td>
<td>0.46</td>
<td>94.54</td>
<td>1.43</td>
<td>2.19</td>
</tr>
<tr>
<td>Avicel Carbon,VM(^e)</td>
<td>NA(^f)</td>
<td>47.48</td>
<td>5.15</td>
<td>46.32</td>
</tr>
</tbody>
</table>

\(^a\)wb= reported on a wet basis. \(^b\)db= reported on a dry basis.
\(^c\)dry basis values by Huffman Hazen Laboratories, a Division of Hazen Research.
\(^d\)Ash by FMC: smaller than 0.05%, Ash by UH via ASTM D3516-89: 0.044%.
\(^e\)VM= Volatile Matter (calculated).
\(^f\)NA= Not Available.

We assumed that the fC content and VM analyzed in every experiment (in accordance with ASTM 1762) had the same composition as the pooled char sample (4.79 MPa, 300\(^\circ\)C HHT) provided to Huffman Hazen Laboratories. Figure 3.9 shows a schematic of the carbon mass balance. All percentages are on a dry weight %.

![Figure 3.9. Schematic of a typical WHTB cellulose carbon mass balance.](image-url)
The carbon balances in Tables 3.15 and 3.16 are calculated by using the procedure below.

The carbon (C) in cellulose (in g) is calculated as:

\[ C_{in\ cellulose\ (g)} = dry\ cellulose\ (g) \times \frac{\%C\ cellulose}{100} \]  

(3.2)

where \( \%C\ cellulose = 44.57\% \), as given by Huffman and Hazen Laboratories

The C in the fC (in g) is calculated as shown below:

\[ C_{in\ fC\ (g)} = \frac{fC\ Content\ (%)}{100} \times dry\ char\ (g) \times \frac{\%C\ Char\ 950}{100} \]  

(3.3)

where \( \%C\ Char\ 950 = 94.54\% \), as given by Huffman and Hazen Laboratories

The C in the VM (in g) is calculated as:

\[ C_{in\ VM\ (g)} = \frac{VM\ Content\ (%)}{100} \times dry\ char\ (g) \times \frac{\%C\ VM}{100} \]  

(3.4)

where \( \%C\ VM = 47.48 \) calculated in equation 3.1

For every experiment we analyze the produced gases and calculate the amount of gases CO and \( CO_2 \) in \( \frac{g}{g_{dry cellulosel}} \). Below we show how to get the C in gases (g) from CO and \( CO_2 \):

\[ C_{in\ gas\ CO\ (g)} = dry\ cellulose\ (g) \times \frac{g\ CO}{g_{dry\ cellulose}} \times \frac{12.01g\ C}{28.01g\ CO} \]  

(3.5)

\[ C_{in\ gas\ CO_2\ (g)} = dry\ cellulose\ (g) \times \frac{g\ CO_2}{g_{dry\ cellulose}} \times \frac{12.01g\ C}{44.01g\ CO_2} \]  

(3.6)

The Carbon (C) mass balance is calculated as follows:

\[ C\ mass\ balance\ (\%) = \frac{C_{in\ fC\ (g)} + C_{in\ VM\ (g)} + C_{in\ gases\ (g)}}{C_{in\ cellulose\ (g)}} \times 100 \]  

(3.7)

The carbon mass balances functioned as a useful tool in determining the successful and carefully executed experiments. Out of 40 WHTB experiments, only 11 were selected, due to the carbon balances.
3.3 Results

The WHTB results section comprises two large tiers. First, the theoretical fC yield for cellulose char was calculated, providing a benchmark for comparing all chars made.

A second section discusses how different operating parameters can attain and exceed this theoretical limit. We evaluated the effect of initial Avicel cellulose moisture content on the WHTB process and its results, the effect of different initial N2 pressures and various HTT of the sand bath on the WHTB process, and the characteristics of the Avicel cellulose chars created.

3.3.1 How effective is our WHTB carbonization process? Thermochemical equilibrium calculations

Overview

Thermochemical equilibrium solvers are used to determine the preferred products of biomass pyrolysis. The values obtained from these simulations allow us to establish a benchmark for comparing experimental fC yields. One of those solvers (and the preferred solver in the R3-Laboratory) is STANJAN, which was used to calculate the mass fraction of solid carbon (which can be converted into an fC yield) at thermochemical equilibrium.

The STANJAN equilibrium solid carbon mass fraction was studied under constant pressure conditions during previous work [6] with the Flash Carbonization unit under various conditions and is shown in Figure 3.10. The yield of carbon (27.7 % at 1 MPa) from cellulose is not affected significantly by varying the (constant) pressure. Reactor temperatures over 400°C favour CO and CO$_2$ fractions while the carbon, water and methane fractions decrease. Part c of Figure 3.10 shows that the absence of oxygen is preferred in order to obtain maximum carbon yields. The 27.7% is considered as the maximum fixed-carbon yield from cellulose.
Figure 3.10. Effects of pressure at a constant temperature of 400°C (a), temperature at a constant pressure of 1 MPa (b), and the air delivery (c) on the mass fraction of different cellulose pyrolysis products after thermochemical equilibrium. Source: [6].

STANJAN solves adiabatic combustion equilibrium calculations numerically in single or multiphase systems. To use STANJAN, the species of each phase must be known, together with their respective
molar fractions. Temperature and pressure are also input parameters. The output consists of the composition of each phase and the thermodynamic properties of the system at equilibrium. For the STANJAN calculations below, we used the species file named comb.sud file.

Seven different STANJAN scenarios were explored in this subsection:

- Theoretical fixed carbon yield of Cowboy oak wood at constant pressure. We compared our outcomes with results from a previous work [1]
- Theoretical fixed carbon yield of Avicel cellulose PH-102 at constant pressure (as if the cellulose was carbonized in the flash carbonization lab reactor).
- Theoretical fixed carbon yields of the Avicel cellulose PH-102 at constant volume with varying $m^3/kg$. For this scenario, 5 different set-ups were tested.
  - Cellulose tightly packed with a 12 ton hydraulic ram
  - Cellulose tightly packed with a 1 ton arbor press
  - Cellulose normally packed (19.18g) in the WHTB
  - Cellulose normally packed (19.18g) in a 10 times larger WHTB
  - Cellulose normally packed (19.18g) in a 100 times larger WHTB

**Theoretical fixed carbon yield of Cowboy oak wood at constant pressure**

Before calculating theoretical fixed-carbon yields of cellulose, previously published cowboy oak wood STANJAN data used in a previous work [1] were reproduced. The theoretical fixed-carbon content at a constant pressure was recalculated for fine cowboy oak wood (Hazen) labelled as number 18 in Table 3 of the previous paper, using the ultimate analysis given in the same table. The weight fraction of the ultimate analysis was converted into a molar fraction using:

\[
Molar\ fraction, \ i(\%) = \frac{weight\ fraction, \ i(\%)}{molar\ mass, \ i (g/mol) \times \frac{mol\ C + mol\ H + mol\ N + mol\ O}{mass_{total}(g)}}
\]  

(3.8)

With $i$ being C, H, N or O.
Table 3.2 shows the elemental composition of Cowboy Oak wood [1].

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction (wt%)</td>
<td>51.63</td>
<td>6.16</td>
<td>41.49</td>
</tr>
<tr>
<td>Molar fraction (%)</td>
<td>33.03</td>
<td>46.96</td>
<td>19.94</td>
</tr>
</tbody>
</table>

Table 3.3. Stanjan input conditions for Cowboy Oak Sawdust at a constant pressure.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Process</th>
<th>Molar Fractions initial reactants</th>
<th>Initial T</th>
<th>Initial P</th>
<th>Output products</th>
<th>Final T</th>
<th>Final P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cowboy Oak</td>
<td>Constant Pressure</td>
<td>C 33.03, H 46.96, O 19.94, N 0.08</td>
<td>673 K, 10 Atm</td>
<td>CO, CO2, NO, NO2, CH4, H2, C(s) H2O, H2O(l)</td>
<td>673 K, 10 Atm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The output of this STANJAN operation can be found in Appendix G for this experiment, with the fixed-carbon yield highlighted in green. The fixed-carbon yield was up to 36.48%. Table 3 in [1] indicated an identical theoretical fixed-carbon yield of 36.5%.

**Theoretical fixed carbon yield of Avicel cellulose at constant Pressure**

The theoretical fixed-carbon yield of Avicel cellulose at constant pressure was calculated as though the flash carbonizer (a constant-pressure vessel) were loaded with cellulose. Table 3.4 shows the elemental composition of Avicel cellulose (on a dry basis) as analyzed by Huffman Hazen Laboratories. Huffman Hazen Laboratories provided results on a mass fraction basis, and molar fractions were calculated. It can be argued that the nitrogen amount is so small that it can be omitted from the calculations, but because Huffman Hazen Laboratories supplied the nitrogen data, the data were used.

83
Table 3.4. Elemental composition of the Avicel cellulose in mass fraction & calculated molar fraction.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction (wt%)</td>
<td>44.57</td>
<td>5.98</td>
<td>49.75</td>
<td>0.01</td>
</tr>
<tr>
<td>Molar fraction (%)</td>
<td>29.10</td>
<td>46.52</td>
<td>0.0056</td>
<td>24.28</td>
</tr>
</tbody>
</table>

Table 3.5 shows the input conditions for STANJAN, which are similar to a typical WHTB experiment at 680 psig (47 atm approx.) and 300°C constant sand bath temperature (data from the WHTB experiment of March 13, 2015). To calculate the amount of moles present in the vessel, we used the 150313 experimental dry weight of 19.18 g of cellulose. In the cowboy oak example above, the molar fraction was used, because the amount of feed was unknown.

Table 3.5. Stanjan input conditions for Avicel cellulose at constant pressure.

<table>
<thead>
<tr>
<th>Feed Type Process</th>
<th>Moles initial reactants</th>
<th>Initial T K</th>
<th>Initial P Atm</th>
<th>Output products</th>
<th>Final T K</th>
<th>Final P Atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel cellulose</td>
<td>C 0.7118</td>
<td>273</td>
<td>47</td>
<td>CO, CO2, NO, NO2, CH4, H2, H2O</td>
<td>673</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>H 1.138</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O 0.5964</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N 0.0001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed-carbon yield equals 29.427% (see Appendix G). Whether using molar fraction or moles, STANJAN will converge to the same answer (29.427% with molar masses and 29.431% with molar fractions). Appendix G includes a mental simulation of a situation in which the cellulose is carbonized under constant pressure with pure nitrogen in the WHTB. This little virtual experiment shows that adding $N_2$ to the STANJAN simulation does not have an effect on the fixed-carbon yield (29.429% instead of 29.427%) as $N_2$ is inert.
Theoretical fixed carbon yields of the Avicel cellulose at constant Volume with varying \( m^3/\text{kg} \).

When simulating a WHTB experiment, in order to arrive at the theoretical fixed-carbon yield, STANJAN must be run in a constant volume (not constant pressure) setting. STANJAN will ask for a specific volume (in \( m^3/\text{kg} \)) from which we can deviate:

- a VERY dense packed bed (same \( m^3 \) as the existing WHTB reactor, but larger kg amount of cellulose loaded; or small \( m^3/\text{kg} \)), to
- a normal dense packed bed,
- a very large (non-existing) reactor with large \( m^3 \).

Using this constant volume setting in STANJAN, the operator will be asked to input an estimated final pressure; we used the peak pressure during the reaction (approximately 120 atm).

\[
Estimated \ final \ pressure = (1741 + 14.7) \ psi = 1755.7 \ psi \approx 120 \ atm \quad (3.9)
\]

When running STANJAN in a constant volume setting and using C, H, O as an input, STANJAN is unable to converge at certain volumes and gives an error output. This can be avoided by adding the amount of \( N_2 \) present in the reactor in the beginning.

**Cellulose tightly packed with a 1 ton arbor press or a 12 ton hydraulic ram** The \( R^3 \)-Laboratory is equipped with a pressing die that makes it possible to compress samples using a 1 ton arbor press or a 12 ton hydraulic ram. Figure 3.11 shows the pressing die used on the left, and the compressed cellulose on the right. The cellulose pill was very rigid, but would delaminate in certain, less compressed places.
Figure 3.11. Pressing die and compressed cellulose.

The 1 ton press allowed us to compress a maximum of 3.8926 g of cellulose in one full die, while the 12 ton ram made it possible to make a 5.0881 g cellulose pill. The volume of the pill was assumed to be identical to the total internal volume of the die, which was filled with water and weighed before and after. Using a density of 998.23 g/L at 20°C, the volume of displaced volume is 3.287 x 10^{-6} m^3. Another possibility is to measure the dimensions of the pill created, but as the pill would crack over several places, it was decided that the volume measurement by water was a more accurate method of determining the volume of the die.

**12 ton hydraulic ram** We calculated the specific volume when the reactor is loaded with the tightest packed cellulose, that is, the cellulose pressed with the 12 ton ram. All of the empty void volume ($V_{void}$ in Figure 3.3) was considered to have been filled with the packed cellulose. The apparent density of the cellulose is:

\[
\text{Cellulose apparent density} \left( \frac{g}{cm^3} \right) = \frac{5.0881g}{3.287cm^3} = 1.548 \frac{g}{cm^3} \tag{3.10}
\]

The amount of cellulose when the whole void volume (0.0524 L) is filled with tightly packed cellulose is:

\[
\text{Mass cellulose}(g) = 1.548 \frac{g}{cm^3} \times 52.4cm^3 = 81.1152g \tag{3.11}
\]

The mass of dry cellulose at 5% moisture content is:

\[
\text{Mass dry cellulose}(g) = 81.1152g \times (1 - 0.05) = 77.06g \tag{3.12}
\]
The masses of C, H, N and O are calculated using the weight percentages of the elements given by Huffman Hazen Laboratories in Table 3.4. The initial nitrogen moles are estimated as though only the active dead volume and the dead volume are available but not the void volume:

\[
n_{N_2} = \frac{P * (V_{ADV} + V_DV)}{RT} = \frac{47 \text{atm} * (0.0131 + 0.0278) L}{0.082 \frac{\text{atmL}}{\text{molK}} * 298K} = 0.0787 \text{ moles} \tag{3.13}
\]

The specific volume is calculated as the reactor volume (0.1258 L) divided by the mass inside the reactor (cellulose + nitrogen mass):

\[
V\left(\frac{m^3}{kg}\right) = \frac{0.1258L}{77.06g \text{ cellulose} + (0.0787 \text{ moles} N_2 * 28 \frac{g}{mol N_2})} = 0.001587 \frac{m^3}{kg} \tag{3.14}
\]

The Stanjan input conditions for this iteration are shown in Table 3.6.

Table 3.6. Stanjan Input conditions for Avicel cellulose at a constant volume for cellulose pressed with a 12 ton ram including nitrogen gas as one of the input reactants.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Process</th>
<th>Moles initial reactants</th>
<th>Initial T</th>
<th>Initial P</th>
<th>Output products</th>
<th>Final T</th>
<th>Specific Volume m3/kg</th>
<th>Estimated Final P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel cellulose</td>
<td>Constant Volume</td>
<td>C 2.860</td>
<td>298</td>
<td>47</td>
<td>CO, CO2, NO, NO2, CH4, H2, H2O</td>
<td>573</td>
<td>0.001587</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 4.572</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 2.396</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 0.00055</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N2 0.0787</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield amounts up to 42.481% (see Appendix G).

\[
Fixed \text{ carbon yield}(\%) = \frac{mass \ fraction \ C(s)}{1 - mass \ fraction \ N_2} \times 100 = \frac{0.41304}{(1 - 0.027714)} \times 100 = 42.481\% \tag{3.15}
\]

**1 ton arbor press**  In this case, the cellulose apparent density equals to:

\[
Cellulose \ apparent \ density\left(\frac{g}{cm^3}\right) = \frac{3.8926g}{3.287cm^3} = 1.184 \frac{g}{cm^3} \tag{3.16}
\]

The amount of cellulose when the whole void volume (0.0524 L) is filled with the cellulose tightly packed:

\[
Mass \ cellulose(g) = 1.184 \frac{g}{cm^3} \times 52.4cm^3 = 62.0416 g \tag{3.17}
\]

And the mass of dry cellulose considering 5% moisture content is:
\[ \text{Mass dry cellulose}(g) = 62.0416g \times (1 - 0.05) = 58.94g \]

The initial nitrogen moles are estimated as though the active dead volume and the dead volume are full, but the void volume is not. Note that this assumption is incorrect, because it assumes the same amount of nitrogen as when the cellulose is packed with the 12 ton hydraulic arm.

\[ n_{N_2} = \frac{P \times (V_{ADV} + V_DV)}{RT} = \frac{47 \text{ atm} \times (0.0131 + 0.0278)L}{0.089 \frac{\text{atmL}}{\text{molK}} \times 298K} = 0.0787 \text{ moles} \]

The specific volume is calculated as the reactor volume (0.1258 L) divided by the mass inside the reactor (cellulose + nitrogen mass):

\[ V \left( \frac{m^3}{kg} \right) = \frac{0.1258L}{58.94g \text{ cellulose} + (0.0787 \text{ moles} N_2 \times 28 \frac{g}{\text{mol} N_2})} = 0.002057 \frac{m^3}{kg} \]

Table 3.7. Stanjan Input conditions for Avicel cellulose at a constant volume for cellulose pressed with a 1 ton press including nitrogen gas as one of the input reactants.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Process</th>
<th>Moles initial reactants</th>
<th>Initial T</th>
<th>Initial P</th>
<th>Output products</th>
<th>Final T</th>
<th>Specific Volume</th>
<th>Estimated Final P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel cellulose</td>
<td>Constant Volume</td>
<td>C 2.187</td>
<td>298</td>
<td>47</td>
<td>CO, CO(_2), NO, NO(_2), CH(_4), H(_2), H(_2)O</td>
<td>573</td>
<td>0.002057</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 3.497</td>
<td></td>
<td></td>
<td>C(s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 1.833</td>
<td></td>
<td></td>
<td>H(_2)O(l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 0.00042</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N2 0.0787</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield equals to 41.62% (see Appendix G).

\[ \text{Fixed carbon yield(\%)} = \frac{\text{mass fraction} C(s)}{1 - \text{mass fraction} N_2} \times 100 = \frac{0.40121}{1 - 0.035948} \times 100 = 41.62\% \]

**Cellulose packed as in a standard experiment (150313 WHTB experiment)** In order to calculate the specific volume during a specific experiment, we mimicked the specific volume of the March 13, 2015 WHTB experiment. This specific volume is calculated by dividing the reactor volume (\(V_{\text{bomb}} + V_{sv}=0.1258\) L) by the mass inside the reactor (cellulose + nitrogen mass):

\[ V \left( \frac{m^3}{kg} \right) = \frac{0.1009L + 0.0249L}{19.18g \text{ cellulose} + (0.21 \text{ moles} N_2 \times 28 \frac{g}{\text{mol} N_2})} = 0.00502 \frac{m^3}{kg} \]
Table 3.8 shows the moles, input and output conditions of the experiment. The moles of nitrogen (0.21 moles) introduced were calculated in the WHTB Excel file for the experiment of March 13, 2015.

Table 3.8. Stanjan Input conditions for Avicel cellulose at a constant volume for 150313 experiment including nitrogen gas as one of the input reactants.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Process</th>
<th>Moles initial reactants</th>
<th>Initial T</th>
<th>Initial P</th>
<th>Output products</th>
<th>Final T</th>
<th>Specific Volume m3/kg</th>
<th>Estimated Final P Atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel cellulose</td>
<td>Constant Volume</td>
<td>C 0.7117</td>
<td>298</td>
<td>47</td>
<td>CO, CO₂, NO, NO₂, CH₄, H₂, H₂O</td>
<td>573</td>
<td>0.00502</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 1.137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0.5964</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 0.000137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ 0.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield equals to 33.188% (see appendix G).

\[
Fixed\ carbon\ yield(\%) = \frac{mass\ fraction\ C(s)}{1 - mass\ fraction\ N₂} \times 100 = \frac{0.25417}{(1 - 0.23416)} \times 100 = 33.188\% \tag{3.23}
\]

Cellulose in a 10 times larger reactor (compared to the 150313 experiment reactor)

To calculate the specific volume as though the reactor were loaded with the same amount of cellulose in a reactor 10 times larger (1.258 L reactor), the initial nitrogen moles are first estimated as the moles in the previous reactor (a 0.1258 L reactor loaded with cellulose, equaling 0.21 moles of nitrogen) plus the moles in a 1.258 L - 0.1258 L reactor calculated with the ideal gas law.

\[
n_{N₂} = 0.21 \text{ moles} N₂ \times \frac{47 \text{ atm} \times (1.258 - 0.1258) L}{0.082 \frac{\text{atm}L}{\text{mol}K} \times 298 K} = 2.39 \text{ moles} \tag{3.24}
\]

The specific volume is calculated as the reactor volume (1.258 L) divided by the mass inside the reactor (cellulose + nitrogen mass):

\[
V\left(\frac{m^3}{kg}\right) = \frac{1.258 L}{19.18 \text{ g cellulose} + (2.39 \text{ moles} N₂ \times 28 \frac{g}{\text{mol} N₂})} = 0.0146 \frac{m^3}{kg} \tag{3.25}
\]
Table 3.9. Stanjan Input conditions for Avicel cellulose at a constant volume reactor 10 times larger than
the 150313 reactor including nitrogen gas as one of the input reactants.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Type</th>
<th>Moles initial reactants</th>
<th>Initial T</th>
<th>Initial P</th>
<th>Output products</th>
<th>Final T</th>
<th>Specific Volume m3/kg</th>
<th>Estimated Final P Atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel</td>
<td>Constant</td>
<td>C 0.7117</td>
<td>298</td>
<td>47</td>
<td>CO, CO₂, NO, NO₂, CH₄, H₂, H₂O</td>
<td>573</td>
<td>0.01461</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Volume</td>
<td>H 1.137</td>
<td></td>
<td></td>
<td>C(s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0.5964</td>
<td></td>
<td></td>
<td>H₂O(l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 0.000137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ 2.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield equals to 29.385% (see appendix G).

\[
Fixed\ carbon\ yield(\%) = \frac{mass\ fraction\ C(s)}{1 - mass\ fraction\ N₂} * 100 = \frac{0.065593}{1 - 0.77678} * 100 = 29.385\% \quad (3.26)
\]

**Cellulose in a 100 times larger reactor (compared to the 150313 experiment reactor)**

For a reactor 100 times larger (a 12.58 L reactor), the initial nitrogen moles are again estimated as
the moles in the previous reactor (a 0.1258 L reactor loaded with cellulose, equaling 0.21 moles of
nitrogen) plus the moles in a 12.58 L - 0.1258 L reactor calculated with the ideal gas law.

\[
n_{N₂} = 0.21\ moles\ N₂ + \frac{47\ atm \times (12.58 - 0.1258)\ L}{0.082\ \text{atm} \text{L} \text{ mol}^{-1} \text{ K}^{-1} \times 298\ K} = 24.16\ moles \quad (3.27)
\]

The specific volume was calculated as the reactor volume (12.58 L) divided by the mass inside
the reactor (cellulose + nitrogen mass)

\[
V\left(\frac{m^3}{kg}\right) = \frac{12.58L}{19.18\ g\ cellulose + (24.16\ moles\ N₂ \times \frac{28\ g}{\text{mol} N₂})} = 0.01808\ \frac{m^3}{kg} \quad (3.28)
\]
Table 3.10. Stanjan Input conditions for Avicel cellulose at a constant volume reactor 100 times larger than the 150313 reactor including nitrogen gas as one of the input reactants.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Process</th>
<th>Moles initial reactants</th>
<th>Initial T (K)</th>
<th>Initial P (Atm)</th>
<th>Output products</th>
<th>Final T (K)</th>
<th>Specific Volume (m3/kg)</th>
<th>Estimated Final P (Atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel cellulose</td>
<td>Constant Volume</td>
<td>C 0.7117</td>
<td>298</td>
<td>47</td>
<td>CO, CO₂, NO, NO₂, CH₄, H₂, H₂O</td>
<td>573</td>
<td>0.01808</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 1.137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0.5964</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 0.000137</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ 24.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield equals to 29.489% (see appendix G).

\[
Fixed \text{ carbon yield} (%) = \frac{mass \text{ fraction } C(s)}{1 - mass \text{ fraction } N₂} \times 100 = \frac{0.0081508}{(1 - 0.97236)} \times 100 = 29.489\% \quad (3.29)
\]

**Results**

Seven different STANJAN simulations were tested and documented above and in the appendix. To verify our STANJAN skills, we carried out a preliminary test in which we succeeded in reproducing a published STANJAN simulation in which cowboy oak sawdust reactant yielded CO, CO₂, NO, NO₂, CH₄, N₂ and H₂O under a constant pressure atmosphere. We then switched to Avicel cellulose reactant, but simulated the same constant pressure reactor conditions. Our final simulations tested constant volume reactors. When we tested cellulose under the experimental conditions used on March 13 (4.79 MPa psig and 300°C HTT), STANJAN could not converge into a solution. When we introduced nitrogen gas as a reactant, STANJAN could solve the problem. Therefore, we did all of the simulations both with and without nitrogen gas as a reactant. As expected, both simulations give very similar results. The Stanjan calculations for C, H and O only are identical to the ones for C, H, N and O with the exception that one does not need to account for the nitrogen present when calculating the fixed carbon yield.
Table 3.11. Stanjan Fixed Carbon Yield Results for the seven processes tested for both with and without N and \( N_2 \) as initial reactants.

<table>
<thead>
<tr>
<th>Process</th>
<th>With ( N_2 ) as gas input</th>
<th>Without ( N_2 ) as gas input</th>
</tr>
</thead>
<tbody>
<tr>
<td>oak Cowboy wood (Constant pressure)</td>
<td>NA</td>
<td>36.48</td>
</tr>
<tr>
<td>Avicel cellulose (Constant Pressure)</td>
<td>29.43</td>
<td>29.43</td>
</tr>
<tr>
<td>12 ton hydraulic ram (Constant Volume)</td>
<td>42.48</td>
<td>42.53</td>
</tr>
<tr>
<td>1 ton arbor press (Constant Volume)</td>
<td>41.62</td>
<td>41.68</td>
</tr>
<tr>
<td>Cellulose (150313) (Constant Volume)</td>
<td>33.19</td>
<td>Failed to converge</td>
</tr>
<tr>
<td>Cellulose (10x V) (Constant Volume)</td>
<td>29.39</td>
<td>29.46</td>
</tr>
<tr>
<td>Cellulose (100x V) (Constant Volume)</td>
<td>29.49</td>
<td>29.57</td>
</tr>
</tbody>
</table>

Figure 3.12 shows the fixed-carbon yields and the final gases for the constant volume experiment simulations. The results used are those from the simulations without nitrogen (last column in Table 3.11), except for the experiment 150313 simulation, due to the convergence error reported by STANJAN. The x-axis is in a logarithmic scale.

Figure 3.12. Effects of changes in specific volume of the WHTB reactor on the products of cellulose pyrolysis after thermochemical equilibrium at 300\(^\circ\)C is reached.
3.3.2 The effect of varying moisture content of the Avicel cellulose on the WHTB process

This section covers the summary of five experiments in which varying Avicel cellulose moisture contents were pyrolyzed using the WHTB in the sand bath (with the sand bath temperature steadily increasing from 300°C to 400°C). The experiments started with a sand bath starting temperature of 300°C. As soon as the WHTB was lowered in the sand bath, all heaters were turned on and the heating set to maximum. The experiment was considered to be completed when the sand bath temperature reached 400°C. An average of 60 minutes was needed to increase the sand bath temperature from 300 to 400°C, making the heating rate rather slow (about 1.67°C/min). All experiments were done in a 2.40 MPa N₂ atmosphere. No vacuum was used to evacuate the WHTB, since this might have influenced the cellulose moisture content before the experiment by lowering the boiling temperature of water. Table 3.12 shows the five WHTB experiments in order of increasing MC.

Table 3.12. WHTB experiments with varying initial Avicel cellulose moisture contents.

<table>
<thead>
<tr>
<th>Experiment Date yymmdd</th>
<th>Initial Avicel cellulose MC %,wb</th>
<th>Sand Bath Heating Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>140226</td>
<td>5[^a]</td>
<td>Constant 300°C</td>
</tr>
<tr>
<td>140625</td>
<td>5[^a]</td>
<td>Gradual Increase</td>
</tr>
<tr>
<td>140624</td>
<td>10</td>
<td>300°C → 400°C</td>
</tr>
<tr>
<td>140619</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>140616</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>140623</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>

\[^a\]Lab equilibrium MC.

Table 3.13 shows the conditions and results for the various experiments, with increasing moisture content from left to right. The weight of Avicel cellulose loaded into the WHTB decreased as the moisture contents increased. Care was taken to avoid leaving any big void spaces inside the cellulose bed; generally, the operator tapped the WHTB during loading. As the MC increased, the cellulose became more cohesive, and could not migrate into the small holes of the TC holder; this could have resulted in the formation of air pockets, especially at the highest moisture content. Cellulose also swells when it comes in contact with water [142]. At the lowest MC level, a lot of cellulose char was found in the TC holder, compared to other runs at higher moisture content levels.
Table 3.13. Comparison of the conditions and results for WHTB experiments with varying cellulose moisture contents (5%, 10%, 14%, 20% and 26%) all under an initial 2.40 MPa nitrogen atmosphere and with the sand bath between 300 and 400°C.

<table>
<thead>
<tr>
<th>Moisture Content [% wb]</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>20</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment Date [yy/mm/dd]</td>
<td>140625</td>
<td>140624</td>
<td>140619</td>
<td>140616</td>
<td>140623</td>
</tr>
</tbody>
</table>

**Reactants**

- Cellulose Moist Mass [g]
  - 19.55
- Cellulose Moisture Content [% wba]
  - 4.62
- Gas Contained in VBomb + VSV [mol]
  - 0.1080

**Pyrolysis Reaction**

- Axis Peak Temperature [°C]
  - 310
- Wall Peak Temperature [°C]
  - 355
- Peak Pressure [MPa]
  - 10.2

**Char Products**

- Char Moist Mass [g]
  - 13.63
- Char Moisture Content [% wb]
  - 5.92
- Char Product Dry Mass [g]
  - 11.34
- Percentage Dry Mass Change [% dbc]
  - 39.2
- Volatile Matter Content [% db]
  - 33.7
- Ash Content [% db]
  - 1.2
- Fixed Carbon Content [% db]
  - 65.1
- Fixed Carbon Yield [% daf]
  - 39.58

**Gas Products**

- Final Gas in VBomb + VSV [mol]
  - 0.187

**Mass Balance**

- Gas Products [% db]
  - 8.73
- Char Yield [% db]
  - 60.81
- Water including Mass of Water on Glass Wool [% db]
  - 27.90
- Total [% db]
  - 97.43

Carrying out an experiment with completely dry cellulose (0% MC) posed additional challenges, as dried cellulose is hygroscopic and will quickly absorb moisture in the R3-Laboratory environment. The WHTB was loaded with cellulose (with a standard lab equilibrated MC of 5%) and pumped to a vacuum for two hours, while the reactor was kept inside the sand bath at 100°C. After the two-hour drying period, the reactor was cooled down (still closed). The typical WHTB procedure was then followed.

A change from 5 to 10% MC decreased the char yield, but increased the fixed-carbon content yield. There was little change in char yield when the MC was increased from 10 to 26%. As
the MC increased, the fixed-carbon content increased, the volatile matter content decreased and
the ash content stayed constant. As expected, larger amounts of gas were produced when the
initial cellulose was wet; regardless of the moisture content, only a certain amount of the water will
contribute to the production of additional gases.

When the cellulose was pyrolyzed at the lab equilibrium moisture content of 5%, the axis
temperature increased beyond and above the wall temperature. In previous reports, we attributed
this to secondary exothermic char reactions. When the moisture content was doubled from 5 to
10%, this overshoot was no longer visible. The axis temperature did show a steeper section where
the overshoot would normally be, which indicates that exothermic reactions were still present.
WHTB experiments at 14, 20 and 26% showed neither the overshoot (of the axis temperature over
the wall temperature) nor the steeper section in the axis temperature.

All experiments, with the exception of the highest MC experiment, reached a final reactor
pressure of around 9.75 MPa when the sand bath reached 400°C. Interestingly, when the reactor
was lifted out of the sand bath after 60 minutes, the pressure started to rise a little. The vibrations
of the hoist caused water to fall from the upper, colder lines in the hot reactor. This showed that
a lot of water was stored in the upper lines.

All of the chars made during these experiments went through a molten phase. Visually, the
outside of the cellulose char tube looked similar for every experiment, with the exception that
more shimmery parts were observed at higher initial cellulose moisture contents. The inside of
each char tube was porous; this porosity appeared to decrease as the initial cellulose MC increased.
At higher moisture contents, the char became rock-hard. Moreover, as the MC increased, the
char tube appeared to expand towards the bottom of the reactor, which could indicate that
the cellulose exhibited fluid characteristics during the experiment. At 10% MC, fluctuations in
the axis temperature were observed from 30 minutes onward. This could be caused by possible
condensation in the WHTB upper lines and boiling of the water in the WHTB reactor. When
enough condensation occurred in the upper lines, water could drip back to the reactor and boil off
again. At higher moisture contents (14, 20 and 26%) this phenomenon was no longer observed.

To verify the separation of water in the hot and cold sections of the WHTB by boiling and
condensing, 10 g of de-ionized water were loaded in the WHTB (using the TC holder and spider,
but no glass or Kao wool).

If we assume quasistatic heating of a closed volume, the pressure at which the last droplet of
water evaporates is calculated as follows. Assuming the 10 g in our WHTB of volume 0.0978L:
\[ v_{\text{max}} = \frac{V_{\text{bomb}}}{m_{H_2O}} = \frac{0.0978L}{10g} \times \frac{1m^3}{1000L} \times \frac{1000g}{1kg} = 0.00978 \frac{m^3}{kg} \] (3.30)

The specific volume of the saturated water at 20°C was 1.0018*10^{-3} \frac{m^3}{kg}. The final pressure with a saturated vapor specific volume equivalent to the maximum specific volume of 0.00978 \frac{m^3}{kg} is the pressure when the last drop of water evaporates. The final pressure was found via interpolation:

\[ P_{v_{\text{max}}} = P_1 + \frac{P_2 - P_1}{v_2 - v_1} \times (v - v_1) = 145.9 \text{bar} + \frac{186.5 \text{bar} - 145.9 \text{bar}}{0.006945 \frac{m^3}{kg} - 0.01080 \frac{m^3}{kg}} \times (0.00978 \frac{m^3}{kg} - 0.01080 \frac{m^3}{kg}) \] (3.31)

which gives us

\[ P_{v_{\text{max}}} = 156.6 \text{bar} = 15.7 \text{MPa} \] (3.32)

The final pressure of the WHTB filled with 10g of water and heated until only saturated water vapor was present was 15.7 MPa. This would be the final pressure assuming thermodynamic equilibrium and a WHTB which does not have colder parts. When steam condenses in the upper colder lines, the water does not contribute to the increased pressure, and the total final pressure is lower.

Figure 3.13 shows the temperature profile of the axis temperature together with the constant sand bath temperature at 300°C when 10 g of water was put in the WHTB.
Figure 3.13. WHTB experiment to verify the behavior of water caused by the hot and cold sections.

The axis temperature profile showed cyclic behavior, varying between 150 and 280°C. Those are close to the evaporation temperatures of water at the present pressures, and the temperature of the sand bath, respectively. This proves that certain amounts of water boiled, rose to the top of the reactor and condensed out. The reactor pressure showed a maximum pressure of 0.38 MPa (40 psig), dropping to 0.32 MPa (31 psig), decreasing slowly but continuously. This was because more condensation than evaporation occurred. At around 24 minutes, the reactor pressure dropped to the equilibrium pressure of 0.29 MPa (27 psig) and the axis temperature rose to the sand bath temperature. This was a sign that the experiment was over and no more extraordinary events would be observed. After the WHTB was removed from the sand bath, the pressure started to rise slightly (37 min). This experiment proved that it is impossible to reproduce the experiments from Mok et al [136] (which used an apparatus with no cold dead volumes) with varying amounts of moisture in cellulose feed with the current WHTB setup.

Under 'real life' circumstances, the water will only evaporate with large enough mass transfer effects at higher temperatures (at higher pressures); hence the water will remain in the cellulose for a while and could have an effect.
New WHTB design for future MC experiments

As we were not sure how much water was contributing to the pyrolysis reactions as a result of the cold and hot sections of the WHTB, a new design was made. All unnecessary volume that was not heated by the sand bath was eliminated. The pressure transducer had to be protected from the hot environment, and the burst diaphragm could potentially be eliminated (along with the sequestered volume) should we reproduce the experiments (and know what the maximum pressure would add up to). Figure 3.14 shows the elimination of the burst diaphragm and excessive lines and valves (compared to Figure 3.3).

Figure 3.14. Upgraded WHTB apparatus for moisture content experiments.
The volume of the WHTB reactor as a whole \( (V_{\text{bomb}}) \) is determined by pressurizing the reactor with the volume of a pressurized air cylinder (0.6L), followed by a depressurization into the water displacement vessel (see Figure 3.5). The weight of water displaced can be converted into a volume by dividing it by the density of water.

The volume of the reactor \( (V_A \text{ or } V_{\text{void}} + V_{\text{ADV}}) \) is measured by filling the reactor with water via a burette. This active volume is the volume of the reactor that is heated. By taking the difference between \( V_{\text{bomb}} \) and \( V_A \), we end up with the volume of the reactor that is 'cold' during an experiment (shaded blue in Figure 3.14).

The new reactor (shown in 3.14) whose not heated volume, was reduced from 0.0603 L (in the original reactor 3.3) to 0.0183 L. The new reactor will be used in future MC experiments, and all results in this thesis are obtained using the original WHTB reactor.

3.3.3 The effect of varying temperatures and pressures on the WHTB process

Over the course of a year and a half, more than 40 WHTB experiments were carried out with varying sand bath treatment temperatures and initial gas pressures. Focus is given to the eleven experiments in Table 3.14, which were conducted at carefully chosen temperatures and pressures. These 11 experiments in Table 3.14 were carried out with the improved moisture content analysis and all had a carbon balance, using the gas, liquid and solid phase date, calculated. The carbon balance should be close to 100% for an experiment to be considered successful. The pressures ranged from atmospheric throughout the experiment (by keeping the valves open, to allow generated gases to escape the WHTB during pyrolysis), to atmospheric initial pressure, to 4.79 MPa. Pressures over 4.79 MPa would yield final pressures too close to the safety limits of the WHTB.

Four sets of sand bath heating regimes were used: a constant 240\(^\circ\)C, 260\(^\circ\)C or 300\(^\circ\)C; and a temperature regime starting at 300\(^\circ\)C increasing gradually to 400\(^\circ\)C. Experiment number nine used a regime starting at 300\(^\circ\)C, increasing to 325\(^\circ\)C, for reasons that will be explained further on.
Table 3.14. List of WHTB experiments conducted at different initial reactor pressures and heat treatment temperatures.

| Experiment # | Date (yy/mm/dd) | Initial $N_2$ Pressure (MPa) | HTT ($^\circ$C) |
|--------------|-----------------|------------------------------|----------------|---|
| 1$^a$        | 150429          | 0.10                         | 300            |   |
| 2            | 150427          | 0.10                         | 300            |   |
| 3            | 150422          | 2.40                         | 240            |   |
| 4            | 150401          | 2.40                         | 260            |   |
| 5$^b$        | 150226          | 2.40                         | 300            |   |
| 6            | 150204          | 2.40                         | 300            |   |
| 7            | 150325          | 2.40                         | 300-400        |   |
| 8            | 150305          | 3.55                         | 300            |   |
| 9            | 150319          | 3.55                         | 300-325        |   |
| 10           | 150311          | 4.79                         | 300            |   |
| 11           | 150313          | 4.79                         | 300            |   |

$^a$Constant atmospheric pressure. $^b$Dry cellulose (0% MC).

The temperature and the reactor pressure of each experiment was carefully recorded and monitored through labVIEW. Figure 3.15 shows the temperature and reactor pressure history of a typical WHTB experiment. This particular experiment had an initial $N_2$ pressure of 4.79 MPa and was plunged into a sand bath of 300$^\circ$C at time 0.

The sand bath heated the WHTB reactor uniformly from the outside (measured by ‘thermocouple wall’) causing the temperature inside the reactor (measured by ‘thermocouple axis’) to increase, with a small time lag. After seven minutes, the temperature of the axis increased above the wall temperature due to an exothermic reaction inside the reactor. This exothermic reaction was caused by formation from cellulose; the increase of axis temperature from 285$^\circ$C to almost 320$^\circ$C, as shown in the inset plot of Figure 3.15 (which displays experiment 11 in Table 3.14), contributed to the pressure increase in addition to the generated pyrolyses gases. The temperature of the wall increased after the exothermic reaction as well, as the reactor lost heat to the sand bath because of its higher temperature.

Typically the WHTB was left in the sand bath for an extra 10 minutes after the exothermic reaction to create experiments that could be compared with each other.
Figure 3.15. Typical temperature profile of a 4.79 MPa WHTB experiment at 300°C HTT. Almost every experiment shows this typical profile with an exotherm observed. No water boiling plateau was observed.

Figure 3.16 shows the temperature and pressure derivatives versus the axis temperature. The derivatives make it possible to observe small changes in axis temperature and reactor pressure. Therefore, the exotherm can be seen more clearly on this graph; it occurred when the axis temperature was between 200 and 250°C (sometimes closer to 275°C). The exotherm was followed by a spike in the pressure derivative. Just before the exotherm the pressure derivative increased as well, which is explained by vigorous devolatilization of the cellulose sample.
Figure 3.16. Temperature and pressure derivatives versus temperature axis of a 4.79 MPa WHTB experiment at 300°C HTT (experiment 11 in Table 3.14).

Figure 3.17 shows the temperature profile of an initial 2.40 MPa pressure experiment during which the sand bath temperature was allowed to increase from 300°C to 400°C during the experiment. This experiment is number 7 in Table 3.14.
Figure 3.17. Typical temperature profile of a 2.40 MPa WHTB experiment with a 300°C-400°C HTT.

Figure 3.18 shows the temperature profile (at a continuous pressure of 0.10 MPa) of experiment number 1 in Table 3.14, without the observation of an exotherm.
Figure 3.18 shows a picture and schematic of an extra thermocouple placed inside the sand bath after 19 April 2015. Before the 19th of April, the sand bath temperature was measured by a thermocouple placed inside a well on the side of the sand bath. This well allows the thermocouple to be right above the heaters. If this thermocouple is not inserted properly and/or if the fluidizing air is not free of water, the temperatures recorded by this thermocouple will be underestimated.

The new thermocouple (supported by an L-shaped 1/4” Swagelok line) measures the temperature of the sand bath next to the WHTB. Differences of 15°C between the two TC inside the sand bath have been observed.
The effect of the initial reactor $N_2$ pressure on the fixed carbon content and fixed-carbon yield of cellulose char is displayed in Figure 3.20. The triangles are the fixed-carbon contents (on the left Y-axis), while the rectangles represent the fixed-carbon yields (on the right Y-axis). Both triangles and rectangles have error bars, because the proximate analysis happens in threefold. Blue symbols indicate experiments done at 300°C while red symbols show experiments at 300-400°C. The yellow symbol is used for the experiment with dry cellulose and the light blue symbols for the experiment carried out with the valves open (atmospheric pressure throughout the experiment). Each symbol is assigned a number that can be found in Table 3.14. When the cellulose char showed evidence that it went through a liquid phase, a symbol is placed next to the designated symbol. A star symbol means that the cellulose did not completely go through the characteristic molten phase.
Only experiments 1, 2 and 3 in Table 3.14 of the series displayed in Figure 3.20 did not go through a molten phase; i.e. the experiments that used an initial atmospheric pressure (whether or not the WHTB valves are closed) and a 240°C sand bath temperature. These two conditions were found to be the pressure and temperature lower limits, which need to be exceeded in order to create char from cellulose that shows evidence of a molten phase. Experiment number 1 in Table 3.14 did not have the typical exotherm, while experiment 2 did. Neither char went through a liquid phase. This shows that the exotherm is caused by the higher initial pressure. The char from experiment 1 had the lowest fC content of 44.6%, followed by an fC of 47.6% for the 240°C experiment. To create a molten-phase char, the temperature in the WHTB should be over 240°C, and the pressure should be allowed to increase. To create a high quality char, it is necessary to have a high initial $N_2$ pressure.

It is clear that increasing the initial $N_2$ pressure causes the fixed-carbon contents and yields to increase, but it is not necessary to increase the pressure over 3.55 MPa as there is a plateau. The fixed-carbon content peaks at higher temperatures, as can be seen from experiment 7. The fixed-carbon content of experiment 9 should have been at least as high as that of experiment 7, but the WHTB never reached temperatures close to 400°C.
Like Figure 3.20, Figure 3.21 shows the effect of the initial reactor $N_2$ pressure on the different char, condensate and gas yields of the WHTB pyrolysis experiments. It can again be observed that the fixed-carbon yield plateaued after 3.55 MPa. The experiment numbers are keyed to Table 3.14. The $CO_2$ yield increased with pressures from 0.10 MPa to 2.40 MPa, after which it reached a plateau. Pressure did not seem to have an effect on the CO yields, while $H_2$ and $CH_4$ were present in such small amounts (and their yields changed so minimally) that they are not visible in the figure. The VM yield decreased slightly as pressure increased, which might indicate more severe conditions at higher pressures. There is no trend observed for the ash yield, partly because of the small amount of ash present relative to the other fractions. With increasing pressure, the char yield increased as well, which partly explained the increase in fixed-carbon yields with increasing pressure.

Figure 3.21. Effects of the initial reactor $N_2$ pressure on the char, condensate and gas yield of the final product after carbonization.
The effect of the HTT of the sand bath on the different yields is visualized in Figure 3.22. Higher sand bath temperatures created conditions that devolatilized the cellulose char sample more. In addition, during the experiments at 240°C, 260°C and 300°C, the WHTB reactor sat in the sand bath for 10 minutes after the exotherm, while the experiments from 300-400°C were terminated as soon as the sand bath reached 400°C. Figure 3.19 shows the temperature and pressure profile of experiment 7 in Table 3.14. As a sample was heated to higher temperatures, more CO₂ was emitted, decreasing the char yield. A peculiar detail was that, for the experiments in which the temperature rose to 400°C, it was harder to collect the char afterwards. This is illustrated in the 'unknown' section of Figure 3.22, which increases as the temperature increases.

![Figure 3.22. Effects of the HTT on the yields of char, condensates and gas products of cellulose pyrolysis.](image)

Table 3.15 shows the values associated with Figure 3.20 and Figure 3.21, but greatly expanded. The char yield was slightly enhanced with increasing pressure, but perhaps more importantly, the fixed-carbon content peaked at 3.55 MPa at 58.8%, which translated in the fC yield of Avicel cellulose pyrolyzed in the reactor peaking at 32.6% at initial N₂ pressures over 3.55 MPa, equaling 98% of the calculated theoretical fixed-carbon yield. The VM and ash contents did not seem to
be influenced by pressure increases. It should be noted, as discussed in section 2.2.1, that char with a VM content over 30% is rarely considered high quality. The ash contents are incredibly high (peaking at 0.7%) from carbonization; when starting with an ash content of 0.044% (and assume the char yield is 30 wt%), we should end up with a maximum of 0.00044/0.3 which gives approximately a 0.15% ash content in the final char sample as a result of up-concentration. The ash contents analyzed were five times higher than anticipated. As discussed earlier, the amount of CO\textsubscript{2} emitted per gram of feed was greatly enhanced and peaked at 3.55 MPa after which it plateaued. Overall, the gas yield increased as the initial N\textsubscript{2} pressure increased.

An initial pressure of 3.55 MPa and 4.79 MPa yielded maximum pressures of 10.4 and 12.1 MPa, respectively. It is also interesting to note that the exothermic reaction caused the axis temperature to rise, but this did not seem to increase as the pressure increased.

The carbon balance of our experiments at different pressures showed us that at higher pressures, there was a better recovery of all the carbon products, as we achieved carbon balances closer to 100 wt% (compared to 92 wt%).
Table 3.15. Comparison of the conditions and results for WHTB experiments with varying initial $N_2$ pressure and with a heat treatment temperature of 300°C.

<table>
<thead>
<tr>
<th>Experiment Number [#]</th>
<th>0.1 MPa</th>
<th>2.40 MPa</th>
<th>3.55 MPa</th>
<th>4.79 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td><strong>Reactants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose Moist Mass [g]</td>
<td>20.10</td>
<td>19.47</td>
<td>20.85</td>
<td>20.19</td>
</tr>
<tr>
<td>Cellulose Moisture Content [%], wb$^a$</td>
<td>5.5</td>
<td>6.0</td>
<td>4.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Gas Contained in VBomb + VSV [mol]</td>
<td>0.0034</td>
<td>0.1030</td>
<td>0.1890</td>
<td>0.2131</td>
</tr>
<tr>
<td><strong>Pyrolysis Reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axis Peak Temperature [°C]</td>
<td>365</td>
<td>324</td>
<td>303</td>
<td>328</td>
</tr>
<tr>
<td>Wall Peak Temperature [°C]</td>
<td>296</td>
<td>299</td>
<td>303</td>
<td>306</td>
</tr>
<tr>
<td>Peak Pressure [MPa]</td>
<td>2.34</td>
<td>7.61</td>
<td>10.4</td>
<td>12.1</td>
</tr>
<tr>
<td><strong>Char Products</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char Moist Mass [g]</td>
<td>11.52</td>
<td>11.64</td>
<td>15.18</td>
<td>13.73</td>
</tr>
<tr>
<td>Char Moisture Content [%], wb$^a$</td>
<td>14.83</td>
<td>25.02</td>
<td>29.32</td>
<td>26.29</td>
</tr>
<tr>
<td>Char Product Dry Mass$^b$[g]</td>
<td>10.18</td>
<td>9.47</td>
<td>11.03</td>
<td>10.71</td>
</tr>
<tr>
<td>Percentage Dry Mass Change [%], db$^c$</td>
<td>46.4</td>
<td>48.2</td>
<td>44.5</td>
<td>44.2</td>
</tr>
<tr>
<td>Volatile Matter Content [%], db$^c$</td>
<td>45.6</td>
<td>42.5</td>
<td>40.5</td>
<td>41.7</td>
</tr>
<tr>
<td>Ash Content [%], db$^c$</td>
<td>0.1</td>
<td>0.5</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Fixed Carbon Content [%], db$^c$</td>
<td>54.3</td>
<td>57.0</td>
<td>58.8</td>
<td>58.3</td>
</tr>
<tr>
<td>Fixed Carbon Yield [%],daf</td>
<td>29.1</td>
<td>29.5</td>
<td>32.6</td>
<td>32.5</td>
</tr>
<tr>
<td><strong>Gas Products</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Gas in VBomb + VSV [mol]</td>
<td>0.037</td>
<td>0.147</td>
<td>0.240</td>
<td>0.253</td>
</tr>
<tr>
<td>Nitrogen [mol %]</td>
<td>13.47</td>
<td>70.87</td>
<td>74.38</td>
<td>80.88</td>
</tr>
<tr>
<td>Oxygen [mol %]</td>
<td>0.71</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Hydrogen [g/g (Dry Feed)]</td>
<td>0.00000</td>
<td>0.00003</td>
<td>0.00002</td>
<td>0.00002</td>
</tr>
<tr>
<td>Methane [g/g (Dry Feed)]</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00001</td>
</tr>
<tr>
<td>Carbon Monoxide [g/g (Dry Feed)]</td>
<td>0.01533</td>
<td>0.01515</td>
<td>0.01791</td>
<td>0.01455</td>
</tr>
<tr>
<td>Carbon Dioxide [g/g (Dry Feed)]</td>
<td>0.05411</td>
<td>0.08809</td>
<td>0.10185</td>
<td>0.10343</td>
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<tr>
<td><strong>Mass Balance</strong></td>
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<td></td>
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<tr>
<td>Gas Products [%], db$^c$</td>
<td>6.97</td>
<td>10.33</td>
<td>11.98</td>
<td>11.80</td>
</tr>
<tr>
<td>Char Yield [%], db$^c$</td>
<td>53.61</td>
<td>51.76</td>
<td>55.45</td>
<td>55.80</td>
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<tr>
<td>Water including Mass of Water on Glass Wool [%], db$^c$</td>
<td>24.34</td>
<td>25.51</td>
<td>26.90</td>
<td>23.46</td>
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<tr>
<td>**Total [%], db$^c$</td>
<td>84.92</td>
<td>87.59</td>
<td>94.33</td>
<td>91.06</td>
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<tr>
<td><strong>Carbon Balance</strong></td>
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<td></td>
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<tr>
<td>Total [%], db$^c$</td>
<td>92.61</td>
<td>92.87</td>
<td>101.0</td>
<td>101.5</td>
</tr>
</tbody>
</table>

$^a$wb= reported on a wet basis. $^b$includes residue collected on glass wool. $^c$db= reported on a dry basis.

Table 3.16 explains Figure 3.22 and goes more into detail. Increasing the HTT resulted in lower char yields (by almost 15%), but as mentioned earlier the fixed-carbon content (or the quality) of
the char should be incorporated into the char yield: the fixed-carbon yield. And because the fixed carbon content increased (and VM content decreased), as the HTT increased from 240°C to 300
400°C, overall the fixed-carbon yield increased from 28.05% to 31.70%.

As expected, more gases were generated when the temperature increased, but there was not much difference between 260°C and 300°C; possibly this was due to the different amounts of cellulose initially loaded (more cellulose will lead to more gas generation). Both the \( \text{CO}_2 \) and CO production increased continuously between 240°C and 300°C to 400°C. The \( \text{H}_2 \) production stayed constant over the different temperature ranges, but when the temperature was increased from 300°C to 400°C, the amount of \( \text{H}_2 \) more than tripled (although still low).

As the temperature increased, unloading in particular became more difficult; this showed in the carbon balance, which decreased when the temperature increased.
Table 3.16. Comparison of the conditions and results for WHTB experiments with varying heat treatment temperatures (240°C, 260°C, 300°C and increasing temperature between 300°C and 400°C) all under an initial 2.40 MPa nitrogen atmosphere.

<table>
<thead>
<tr>
<th>Experiment Number [#]</th>
<th>240°C</th>
<th>260°C</th>
<th>300°C</th>
<th>300-400°C</th>
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<tbody>
<tr>
<td>Reactants</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose Moist Mass [g]</td>
<td>19.94</td>
<td>21.27</td>
<td>19.47</td>
<td>20.89</td>
</tr>
<tr>
<td>Cellulose Moisture Content [%], wb&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.4</td>
<td>5.0</td>
<td>6.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Gas Contained in VBomb + VSV [mol]</td>
<td>0.1046</td>
<td>0.0931</td>
<td>0.1030</td>
<td>0.1043</td>
</tr>
<tr>
<td>Pyrolysis Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axis Peak Temperature [°C]</td>
<td>257</td>
<td>286</td>
<td>324</td>
<td>392</td>
</tr>
<tr>
<td>Wall Peak Temperature [°C]</td>
<td>250</td>
<td>271</td>
<td>299</td>
<td>395</td>
</tr>
<tr>
<td>Peak Pressure [MPa]</td>
<td>5.60</td>
<td>6.45</td>
<td>7.61</td>
<td>9.76</td>
</tr>
<tr>
<td>Char Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char Moist Mass [g]</td>
<td>17.72</td>
<td>18.29</td>
<td>11.64</td>
<td>11.80</td>
</tr>
<tr>
<td>Char Moisture Content [%], wb</td>
<td>37.12</td>
<td>36.83</td>
<td>25.02</td>
<td>25.41</td>
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<tr>
<td>Char Product Dry Mass&lt;sup&gt;b&lt;/sup&gt;,[g]</td>
<td>7.69</td>
<td>11.70</td>
<td>9.47</td>
<td></td>
</tr>
<tr>
<td>Percentage Dry Mass Change [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>40.8</td>
<td>42.1</td>
<td>48.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Volatile Matter Content [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>52.3</td>
<td>49.1</td>
<td>42.5</td>
<td>30.7</td>
</tr>
<tr>
<td>Ash Content [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Fixed Carbon Content [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>47.4</td>
<td>50.5</td>
<td>57.0</td>
<td>68.9</td>
</tr>
<tr>
<td>Fixed Carbon Yield [%], daf</td>
<td>28.05</td>
<td>29.24</td>
<td>29.50</td>
<td>31.70</td>
</tr>
<tr>
<td>Gas Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Gas in VBomb + VSV [mol]</td>
<td>0.138</td>
<td>0.130</td>
<td>0.147</td>
<td>0.181</td>
</tr>
<tr>
<td>Nitrogen [mol %]</td>
<td>76.52</td>
<td>70.16</td>
<td>70.87</td>
<td>57.43</td>
</tr>
<tr>
<td>Oxygen [mol %]</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Hydrogen [g/g (Dry Feed)]</td>
<td>0.00001</td>
<td>0.00003</td>
<td>0.00003</td>
<td>0.00011</td>
</tr>
<tr>
<td>Methane [g/g (Dry Feed)]</td>
<td>0.00000</td>
<td>0.00002</td>
<td>0.00000</td>
<td>0.00001</td>
</tr>
<tr>
<td>Carbon Monoxide [g/g (Dry Feed)]</td>
<td>0.00745</td>
<td>0.01062</td>
<td>0.01515</td>
<td>0.02885</td>
</tr>
<tr>
<td>Carbon Dioxide [g/g (Dry Feed)]</td>
<td>0.07331</td>
<td>0.09005</td>
<td>0.08809</td>
<td>0.13812</td>
</tr>
<tr>
<td>Mass Balance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Products [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.08</td>
<td>10.07</td>
<td>10.33</td>
<td>16.71</td>
</tr>
<tr>
<td>Char Yield [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>59.23</td>
<td>57.89</td>
<td>51.76</td>
<td>45.94</td>
</tr>
<tr>
<td>Water including Mass of Water on Glass Wool [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>31.76</td>
<td>30.41</td>
<td>25.51</td>
<td>25.76</td>
</tr>
<tr>
<td>Total [%], db&lt;sup&gt;c&lt;/sup&gt;</td>
<td>99.07</td>
<td>98.37</td>
<td>87.59</td>
<td>88.42</td>
</tr>
</tbody>
</table>

<sup>a</sup>wb= reported on a wet basis. <sup>b</sup>includes residue collected on glass wool. <sup>c</sup>db= reported on a dry basis.
The most fascinating part of the cellulose carbonization in the WHTB, is that we load the cellulose as a powder and unload a solid black piece of char that clearly shows characteristics of fusion and a phase change.

Figure 3.23 shows cellulose char that did not show phase change phenomena in experiment 1 as listed in Table 3.14. The cellulose char from experiment 1, 2 and 3 resembled black flour-like powder and which we were able to pour freely out of the WHTB reactor. Despite the fact that no molten phase was observed, the whole char sample was carbonized.

Figure 3.24 shows the cross-section of the cellulose char tube made at a HTT of 260°C (this is experiment 4 in Table 3.14). The char had gone through a liquid phase (the experiment done at a HTT of 240°C did not), without too much shrinkage of the char, which had a high VM content. The cross-section is very uniform in texture, in contrast to higher temperature and/or higher pressure WHTB experiments.
Figure 3.24. Cellulose char made at a HTT of 260°C.

Figure 3.25 shows the inner and outer layers of the char gradually changing from matte black on the outside, to a shiny inner surface as shown on the picture on the left. The picture on the right shows the char tube, which typically cracks and shrinks mainly in the middle (this is char from experiment 8 in Table 3.14)
As the cooking times get longer (as is the case in the 300-400°C HTT experiments), the char becomes so hard it is impossible to break by hand. As pressures increase, the inside radius of the char tube shows a very rough surface (with the appearance of small craters), as if gases were vigorously trying to boil out of the cellulose sample. Regardless of pressure, the outside usually looks very smooth as can be seen in Figure 3.26 which displays the cellulose char from experiment 11 in Table 3.14.
3.4 Future work

The successful pioneering work performed with the WHTB, which will be continued using different lignocellulosic feeds, was the starting point for launching a new design and scale-up of the constant volume WHTB reactor. This scale-up would be similar to the scale-up from the FC lab-scale reactor into the FC demo-scale reactor. The design and build of the small Swagelok WHTB vessel and the necessary calculations are elaborated in the Swagelok manual [143] and the reduced pressure ratings (because of elevated temperatures) are shown in section 3.2.1.

Together with Matt Austin, I contributed to design a pressure vessel that will receive an ASME U-stamp which represents ASME’s section VIII ‘Division 1’; rules for the construction of pressure vessels. Tubeturns will be manufacturing the vessel using the following specifications:

- 36” long pipe Schedule 80 SA106 B with diameter 12”
- The pipe flanged at the bottom with a class 900 flange and on top with a class 900 Quick-opening
- Installation of 14 1” NPT SA 105 3000 couplings. One on top quick opening, one on bottom and 12 on side of pipe.
- Max temperature of 316°C.

The MAWP is the maximum pressure based on the design codes that the weakest component of a pressure vessel can handle. A carbon steel class 900 unit (for the flange and quick-opening) can handle pressures of 1640 psi (11.4 MPa) [144].

The MAWP is calculated as shown below:

\[
MAWP = \frac{T \times t \times e}{R \times F}
\]

With T= tensile strength of the metal used, which is 60,000 psi for SA106B, t= the minimum thickness of the pipe ("), which is 0.688" if we use a 12” diameter, schedule 80 pipe, e= the efficiency, R= inside radius (”) and F= safety factor, usually 4. The efficiency e is a derating because of holes made in the pipe. We will be making 12 holes in the pipe, but as they are 1” in diameter, the ASME code allows us to use an efficiency of 1.

The MAWP is calculated as shown below:

\[
MAWP = \frac{60,000psi \times 0.688" \times 1}{5.687" \times 4} = 1815psi \text{ or } 12.6MPa
\]

The maximum pressure of the flange/quick-opening is lower than 1815 psi (12.6 MPa), as a result the MAWP becomes the maximum pressure of the flange/quick-opening: 1640 psi (11.4 MPa).
CHAPTER 4
OVERALL CONCLUSIONS

4.1 FC lab scale sewage sludge experiments

1. The decision of the Oahu city administration to close down the Waimanalo Gulch solid waste landfill and concerns as to the timely deployment of a third sewage sludge combusting boiler at H-Power, necessitated urgent measures aimed at reducing the use of landfills through increased recycling and waste-to-energy technologies. The FC lab-scale reactor could carbonize sewage sludge with fC yields up to 28.6%, resulting in final biochar having high ash contents (ranging between 61 and 80%, with a maximum of 90%) whose uses were investigated.

2. The presence of high concentrations of heavy metals (Zn, Mo and Cr) in the biochar rendered the sewage sludge biochars not suitable for land application in Hawaii. The exact physico-chemical properties of the metals and thus the bioavailabilities are unknown.

3. The analysis of heavy metals is rather complex, as there is no uniform standard as to how to separate heavy metals from a certain matrix and as to what analyzer to use. Ranges between 0.46 mg/kg to 15.19 mg/kg for lead were observed in the FC condensates, as analyzed by three reputable laboratories.

4. Sewage sludge could be put to use and possibly be "mined" for its heavy metals. The amounts of Cu in the Hawaii Kai sewage sludge could easily create revenue, which would make sewage sludge an attractive option worth considering.

4.2 FC lab scale Norwegian wood experiments

1. Changes in the FC lab-scale canister diameter and insulation greatly influence charcoal and fixed carbon yields. Our experiments have shown that both the charcoal and fixed carbon yields drop (for example at 0.79 MPa, the charcoal and fixed carbon yield drop from 33.5% to 28.0% and from 26.9 to 23.5%, respectively) when a smaller canister (3.5” OD, an area decrease of 2.4, with more insulation) is being used.

2. The results of the GROT carbonization experiments are promising. Feeds that are very heterogeneous in texture such as GROT could be carbonized with the FC apparatus delivering charcoal yields of 37%. In comparison with their respective wholesome wood, a decrease in charcoal and fixed carbon content (a drop from 31.1 to 25.5%) was observed. The GROT charcoals contained large amounts of ash up to 4.9%, as a result of the high ash contents of the feed.
3. Increased pressure enhanced the fixed-carbon yield of charcoal from wood. An increase in pressure from 0.79 to 2.17 MPa increased the fixed-carbon yield of spruce and birch wood from 27.0% to 31.2% and from 21.9% to 31.2%, respectively. The increase in yield implies high cost savings benefiting the ferrosilicon industry.

4.3 FC demo scale macadamia nutshell experiments

1. The FC demo reactor was capable of fully carbonizing a 50 kg macadamia nut bed into extremely pure fixed carbon charcoal in a time frame of 2 hours without any visible smoke emissions, by a proper synchronization of the retrofitted thermal afterburner to the FC reactor.

2. Larger fC contents (and lower charcoal and fC yields) when using the FC lab scale reactor are equally well achieved using the FC-demo reactor, the improved insulative capacities of which are able to create a charcoal with fC contents of 97%. Because of low charcoal yields, the fC yields only amount up to 24.5% in contrast to earlier work with the FC lab scale reactor generating fC yields of 34%.

3. Future work involves increasing the charcoal yield during the carbonization process and automating the thermal afterburner, consequently ameliorating the user-friendliness of the Flash Carbonization process. A newly designed downdraft valve will soon be tested and allow fine-tuning of the effluent gases to the afterburner

4.4 WHTB Avicel cellulose experiments

1. A trial has been conducted to analyze the effect of water on the charcoal and fixed carbon yields using the WHTB apparatus. As the device is not evenly heated (there is a cold and hot part, see figure), water is allowed to condense in the upper cold parts of the WHTB. It is too early to formulate definite conclusions as yet, but with the new upgraded WHTB, new experiments should be conducted, taking care in loading equal amounts of cellulose, as cellulose is stickier when wet, and therefore harder to load in equal amounts.

2. An increase in initial $N_2$ reactor pressure resulted in an increase of the fC yield up to a maximum of 32.6% at 3.55 MPa, whereafter the fC yield reached a plateau. Operation at initial $N_2$ pressures of 3.55 MPa and 4.79 MPa results in fC yields (32.6% and 31.3%) that attain 98.2 and 94.2% of the theoretical maximum (calculated by STANJAN: 33.19%). Operating under atmospheric conditions in the WHTB apparatus yields 83.0% of the theoretical maximum (29.34%).

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3. An increase in HTT resulted in a decrease of the char yields by almost 15%, and an increase of the fC yield from 28.05% to 31.70%. Lower temperature (260°C HTT) and pressure limits (2.14 MPa initial $N_2$ pressure) have been established in order to create a cellulose char that shows signs of a molten phase.

4. The ash contents of the cellulose chars are unusually high and five times larger than anticipated.


[79] Thiago de Paula ProtasioI; Paulo Fernando TrugilhoII; Seyedmohammad MirmehdiII; Marcela Gomes da SilvaIII. Quality and energetic evaluation of the charcoal made of babassu nut residues used in the steel industry. *Cinc. agrotec.*, 38, 2014.


[93] Daniel Fenning and Joseph Collyer. *A new system of geography: or, A general description of the world. Containing a particular and circumstantial account of all the countries, kingdoms, and states of Europe, Asia, Africa, and America... With the birds, beasts, reptiles, insects, the various vegetables, and minerals, found in different regions*. London Printed, 1770.


[132] Sigma Aldrich. 316555 aldrich.


[159] NIST. Nist guide to the si units, 2015.


APPENDIX A
STANDARD OPERATING PROCEDURES FOR THE THERMAL AFTERBURNER
Procedure THERMAL AFTERBURNER FOR FC
By sam van wesenbeeck
(LP: Lloyd Paredes, NP: Nay Photistantiskul, MLA: Maider Legarra Arizaleta: SVW: Sam Van Wesenbeeck)
Date: 11 September 2014

**Safety:**
Operators and bystanders should wear: glasses, coverall, earmuffs (if 15 kW generator is on), gloves, closed shoes.

**Ground-control SVW and LP:**
Check the connection to the ground with a multimeter by metering the resistance of the line. The resistance should be zero between the grounded copper line and the equipment! If the multimeter does not read zero, repair connection first. Note: some surface oxidation might occur on the line. You can scratch or use sandpaper to clean the line to get better connection with the multimeter. Check the connection points for corrosion.

**Set-up SVW and LP:**
1) Have the propane tank connected to the afterburner (with a one way valve in between valves V2 and V3, see figure 1)
2) Have the ignition system properly grounded and set up on the afterburner. The ignition system should be connected to the 2 spark-plugs.
3) Open the ball valve V4 of the primary air input line fully.
4) Have the blower (opposite from the propane gas input line) running and its ball valve V5 closed. The small Honda (red) 1.5 kW generator can NOT supply enough power for this blower. Use the bigger (and louder) 15 kW generator.

**Set-up NP & MLA:**
1) Place CO/O₂ measurement station on a safe place with help from LP/SVW and make the necessary connections. Small flames might come out of the opening from V4 so do not place the measurement station in this area.
2) Measurements will be taken after stable conditions are obtained in the afterburner. Multiple measurements have to be taken and if conditions change, LP/SVW will signal for additional measurements (NP records changing gas composition, SVW records changing conditions in the afterburner using the same stopwatch for correct time)
3) Keep track of rising CO concentrations and disconnect meters if critical values are reached (this is good training for an actual FC run)
Start afterburner:
1) Open valve V1 of the propane tank and set the pressure regulator (R) to 30 psi (LP)
2) Open valve V3 fully (this was the ON/OFF valve when the flowmeter was attached) (LP)
3) Open the needle valve V2 of the propane tank 1/8 of a turn (LP)
4) Go to the ignition switch and push the button (you will hear a clicking noise, if not, turn down the propane and check ignition system) until the propane/air mixture ignites. Ignition can be noticed visually (with side mirror), by hearing a WHOOOMP when the stack is not in place or by reading out the temperature difference by a TC in the vicinity of the flame (NOT IN THE FLAME). The view port (see figure 1) on the side of the thermal afterburner can be used as well. (SVW)
5) If ignition occurred, go back to the propane tank and open the needle valve V2 of the propane tank to a total of ¼ turn-½ turn (when stack is in place, ½ turn might extinguish the flame). The flame will become bigger/more intense. (SVW)
6) Walk to the blower (bend down because the flame will become bigger at first when you open the air blower valve V5) and open the air blower valve V5 slowly until setting 2. At around setting 2, the flame will get sucked into the mixing chamber. When you reach setting 3, chance of blowing out the flame exists. You will hear the typical sound of a hot and vortexing flame. (SVW)

Stop afterburner:
1) Close the needle valve V1, V2 and V3 (in that order) of the propane tank (LP)
2) Let the air blower cool down the afterburner if needed. If you open the valve V5 of the blower too much (above setting 2) at this time, hot parts might get blown out.
3) Disassemble equipment (all)
Figure 1: Topview of the Flash Carbonization (FC) unit and the thermal afterburner. Valves (V) are numbered. V6 is the valve that allows gases from the FC to enter the thermal afterburner. The 2 viewports are spaced 30 cm from each other and the TC are deliberately placed close (but not in) the propane flame.
APPENDIX B
SEWAGE SLUDGE CARBONIZATION FOR BIOCHAR APPLICATIONS. FATE OF HEAVY METALS
Sewage Sludge Carbonization for Biochar Applications. Fate of Heavy Metals

Sam Van Wesenbeeck,† Wolter Prins,‡ Frederik Ronsse,‡ and Michael Jerry Antal, Jr.*†

†Hawaii Natural Energy Institute, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States
‡University Ghent, Biosystems Engineering, Coupure Links 653, 9000 Gent, Belgium

ABSTRACT: Biochars produced from sewage sludge show promise for use as soil amendments that could both enhance plant growth and sequester carbon. In a previous study, we showed that moist sewage sludge obtained from a rural, residential region of Oahu, Hawaii, could be carbonized, and the heavy-metal content of its biochar did not exceed United States EPA regulations limiting its use as a soil amendment. In this paper, we show that biochars produced from the nearby residential community of Hawaii Kai cannot be used as a soil amendment in Hawaii because their contents of Zn, Mo, and Cr exceed state regulations. Likewise, their contents of Cd, Cu, Ni, and Zn exceed Belgian regulations. These heavy metals are retained in the biochar during carbonization, whereas Hg and (to a lesser extent) As, Cd, and Se are released and thereby depleted in the biochar. Biochar within the carbonizer does not adsorb the heavy metals which are released during pyrolysis; consequently, these leave the carbonizer in its exhaust stream.

1. INTRODUCTION

In a previous paper,1 we at the University of Hawaii presented promising results from a preliminary study of Hawaiian sewage sludge carbonization for biochar soil amendment applications. Our findings showed that sewage sludge from the Honouliuli (“Ewa”) wastewater treatment plant (WWTP) with moisture contents as high as 30 wt % can be carbonized and that the heavy-metal content of its biochar product did not exceed United States EPA regulations for use as a soil amendment. The addition of sewage sludge biochar to the soil can enhance plant growth2 and simultaneously sequester carbon;3 however, its heavy-metal content varies from one community to another, and its use as a soil amendment is controlled implicitly by both federal and state regulations concerning the addition of heavy metals to the soil in the USA and similarly by European Union and country regulations in the EU. To gain further insight into the release and uptake of heavy metals during the carbonization of sewage sludge, and to better quantify the variability of the heavy-metal content of the sludge from one residential neighborhood to another, we undertook this study of the carbonization of Hawaii Kai sewage sludge (HK SS).

With a population of more than 220,000 people,4 Hawaii Kai is the largest residential community on the eastern side of the island of Oahu, Hawaii. The Hawaii Kai WWTP receives wastewater from the eastern ridge of Kuliouou Valley to the Kalanianole Highway at Sandy Beach. This wastewater is mainly residential in origin, apart from a small amount of commercial wastewater originating from three shopping centers, restaurants, various plant nurseries, and a few other facilities (e.g., schools, a golf course, and a shooting range). Oahu’s wastewater system is separated from its stormwater system;5 therefore, no heavy-metal contamination from road deposits is possible.6 Oahu does not have any major industries; the heavy-metal inputs are mainly from agricultural pesticides and fertilizers.7 Despite the increased As concentration in soils of former sugar cane fields in Oahu, no As has been detected in the drinking water system.8 Up to 80% of the heavy metals present in wastewater migrates to the sewage sludge during wastewater treatment.9 These heavy metals are accumulated in different chemical species via biosorption10 on the cell surfaces present in the sewage sludge and are easy to leach out.

The Hawaii Kai WWTP employs primary, secondary, and tertiary treatment. Wastewater is screened before entering a primary clarifier. The supernatant of the primary clarifier is aerobically treated before being pumped to a secondary clarifier. Additional sand filtration and chlorine disinfection are accomplished before the treated water is discharged into the Pacific Ocean. The settled sludge of the primary clarifier is pumped into an anaerobic digester, together with mechanically dewatered settled sludge from the secondary clarifier. The digested sludge is sun dried on gravel beds to reduce costs of landfilling that can exceed $91 per ton wet sewage sludge.11 The digested sludge forms the material of interest for carbonization in this study.

2. APPARATUS AND EXPERIMENTAL PROCEDURES

Sewage sludge samples (SS1, SS2, and SS3) were collected from the surface of the gravel bed during the months of June 2011, September 2011, and October 2012, respectively. Table 1 displays ultimate analyses (i.e., elemental analyses) of SS1 and SS2 together with their biochars. In Table 1 the oxygen content is determined by difference; consequently it is subject to the analytical uncertainty of all of the other components. It is not unusual to see a total above 100% for the other materials. In this case, the oxygen content is listed as <0.01. The ash content of the HK SS is twice that of the Ewa sludge from the
western side of Oahu\textsuperscript{1} but similar to that of Urban and Antal,\textsuperscript{12} Shao et al.,\textsuperscript{13} and Pinto,\textsuperscript{14,15} and less than that of Aznar et al.,\textsuperscript{16} and Fonts et al.\textsuperscript{17} When the desired amount of air was delivered, the air flow was halted. The oxygen concentration in the effluent gas was monitored by an oxygen analyzer (Bacharach, Inc., model OXORII) and recorded. The amount of delivered air was calculated from the pressure levels of the accumulator before and after the experiment. After the carbonization experiment, the reactor was depressurized and cooled, and the solid products were removed for analysis. The biochar product was divided into three sections (i.e., top, middle, and bottom) and equilibrated for 24 h in the open air in the laboratory prior to analysis. The biochar in each section was weighed and a representative sample from each section was subjected to proximate analysis according to ASTM standard D1762-84.

Prior to each run, the moisture content of the corncob and sewage sludge feeds were determined according to ASTM standard E 1756-08. Heavy-metal analyses of both the raw sewage sludge and sewage sludge biochar were obtained from 3 EPA accredited laboratories in the USA (Hazen Research, TestAmerica Laboratories, and FQ Laboratories), and the Laboratory of Analytical Chemistry and Applied Ecochemistry, Ghent University. Only those heavy metals which are subject to regulations in the United States and the European Union for sewage sludge biochar disposal on land were quantified. The regulated heavy metals are As, Cd, Cu, Pb, Hg, Mo, Ni, Se, Zn, and Cr. To study the migration of heavy metals within the reactor, we obtained heavy-metal analyses from the top and a mixture of the middle and bottom biochars of Run 2. We also obtained heavy-metal analyses of the corncob tinder and its biochar from Run 2 and 5.

The analyses by TestAmerica Laboratories and FQ Labs employed ICP-MS in accordance with EPA method 6020.\textsuperscript{24} TestAmerica Laboratories quantified Hg via the EPA method 7471A.\textsuperscript{25} Hazen Research used the EPA series ’7000 methods for As,\textsuperscript{26} Cd,\textsuperscript{27} Cu,\textsuperscript{28} Pb,\textsuperscript{29} Hg,\textsuperscript{30} Ni,\textsuperscript{31} Se,\textsuperscript{32} Zn,\textsuperscript{33} and Cr,\textsuperscript{34} except for Mo\textsuperscript{35} that was analyzed by ICP-AES. Ghent University analyzed Hg by a Cetac mercury analyzer, while the other the heavy metals were analyzed by a combination of ICP-OES and ICP-MS. As a rule of thumb, ICP-MS is said to enjoy the best detection limits.\textsuperscript{36} The outcome of these analyses is strongly influenced by the method of sample digestion employed by each laboratory. FQ Labs used EPA method 3051A\textsuperscript{37} (acid digestion by HNO\textsubscript{3} and/or HCl with microwave assist) that is declared to be the most vigorous method\textsuperscript{38} used for digesting samples because it employs temperatures up to 175 °C and elevated pressures.

### Table 1. Ultimate Analyses\textsuperscript{a} of Sewage Sludge Feeds and Biochars (wt %, dry)

<table>
<thead>
<tr>
<th>batch</th>
<th>feed/biochar</th>
<th>C</th>
<th>H</th>
<th>O\textsuperscript{b}</th>
<th>N</th>
<th>S</th>
<th>ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS\textsuperscript{1}</td>
<td>SS\textsuperscript{1} feed</td>
<td>37.67</td>
<td>5.22</td>
<td>14.59</td>
<td>7.05</td>
<td>3.58</td>
<td>31.89</td>
</tr>
<tr>
<td>SS\textsuperscript{1}</td>
<td>SS\textsuperscript{1} char</td>
<td>30.24</td>
<td>1.29</td>
<td>&lt;0.01</td>
<td>3.13</td>
<td>3.81</td>
<td>64.17</td>
</tr>
<tr>
<td>SS\textsuperscript{2}</td>
<td>SS\textsuperscript{2} feed</td>
<td>37.93</td>
<td>4.90</td>
<td>16.48</td>
<td>7.24</td>
<td>3.59</td>
<td>29.86</td>
</tr>
<tr>
<td>SS\textsuperscript{2}</td>
<td>SS\textsuperscript{2} char</td>
<td>25.30</td>
<td>0.12</td>
<td>&lt;0.01</td>
<td>2.10</td>
<td>4.42</td>
<td>73.43</td>
</tr>
<tr>
<td>SS\textsuperscript{2}</td>
<td>SS\textsuperscript{2} char/T/M\textsuperscript{1}</td>
<td>31.17</td>
<td>0.38</td>
<td>&lt;0.01</td>
<td>2.92</td>
<td>4.17</td>
<td>64.90</td>
</tr>
<tr>
<td>CC\textsuperscript{1}</td>
<td>CC\textsuperscript{1} feed</td>
<td>48.66</td>
<td>5.75</td>
<td>42.19</td>
<td>0.51</td>
<td>0.06</td>
<td>2.83</td>
</tr>
<tr>
<td>CC\textsuperscript{1}</td>
<td>CC\textsuperscript{1} char</td>
<td>77.32</td>
<td>3.16</td>
<td>10.72</td>
<td>2.02</td>
<td>0.59</td>
<td>6.19</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Hazen. \textsuperscript{b}Oxygen calculated by difference. \textsuperscript{1}SS1 = sewage sludge run done on 110626, SS2 = sewage sludge run 2. \textsuperscript{CC} = Corncob. \textsuperscript{T/M} = top and middle of FC reactor. \textsuperscript{B} = bottom of reactor.

### Table 2. Main Ash Elements\textsuperscript{a} of Sewage Sludge and Corncob Feeds and Biochars (wt %, dry)

<table>
<thead>
<tr>
<th>batch</th>
<th>feed/biochar</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>TiO\textsubscript{2}</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>CaO</th>
<th>MgO</th>
<th>Na\textsubscript{2}O</th>
<th>K\textsubscript{2}O</th>
<th>P\textsubscript{2}O\textsubscript{5}</th>
<th>SO\textsubscript{3}</th>
<th>Cl</th>
<th>CO\textsubscript{2}\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS\textsuperscript{1}</td>
<td>SS\textsuperscript{1} feed</td>
<td>13.41</td>
<td>4.79</td>
<td>1.17</td>
<td>23.29</td>
<td>9.11</td>
<td>3.69</td>
<td>8.44</td>
<td>2.36</td>
<td>21.26</td>
<td>12.50</td>
<td>0.36</td>
<td>0.06</td>
</tr>
<tr>
<td>SS\textsuperscript{1}</td>
<td>SS\textsuperscript{1} char</td>
<td>14.44</td>
<td>5.68</td>
<td>1.39</td>
<td>21.24</td>
<td>9.13</td>
<td>3.99</td>
<td>8.61</td>
<td>2.13</td>
<td>20.86</td>
<td>11.90</td>
<td>0.40</td>
<td>0.02</td>
</tr>
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<td>SS\textsuperscript{2} feed</td>
<td>13.96</td>
<td>5.27</td>
<td>1.34</td>
<td>22.53</td>
<td>8.82</td>
<td>4.21</td>
<td>5.37</td>
<td>1.50</td>
<td>24.14</td>
<td>11.80</td>
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<td>NA</td>
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<tr>
<td>SS\textsuperscript{2}</td>
<td>SS\textsuperscript{2} char</td>
<td>14.22</td>
<td>5.17</td>
<td>0.25</td>
<td>5.41</td>
<td>1.79</td>
<td>2.64</td>
<td>7.19</td>
<td>36.90</td>
<td>10.07</td>
<td>2.84</td>
<td>10.08</td>
<td>2.84</td>
</tr>
<tr>
<td>SS\textsuperscript{2}</td>
<td>SS\textsuperscript{2} char/T/M</td>
<td>15.08</td>
<td>5.69</td>
<td>1.19</td>
<td>22.41</td>
<td>9.67</td>
<td>4.31</td>
<td>5.50</td>
<td>1.58</td>
<td>23.94</td>
<td>10.08</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>CC\textsuperscript{1}</td>
<td>CC\textsuperscript{1} feed</td>
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<td>5.24</td>
<td>1.33</td>
<td>21.95</td>
<td>9.00</td>
<td>4.40</td>
<td>5.47</td>
<td>1.62</td>
<td>23.41</td>
<td>11.49</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>CC\textsuperscript{1}</td>
<td>CC\textsuperscript{1} char</td>
<td>32.79</td>
<td>1.57</td>
<td>0.25</td>
<td>5.25</td>
<td>2.72</td>
<td>2.78</td>
<td>0.25</td>
<td>23.70</td>
<td>12.77</td>
<td>13.67</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Hazen. \textsuperscript{b}CO\textsubscript{2} originates from residual C in the form of carbonates and carbonic acid. \textsuperscript{1}SS1 = sewage sludge run done on 110626, SS2 = sewage sludge run 2. \textsuperscript{CC} = Corncob. \textsuperscript{NA} = not analyzed. \textsuperscript{T/M} = top and middle of FC reactor. \textsuperscript{B} = bottom of reactor.
Table 3. Experimental Conditions and Results

<table>
<thead>
<tr>
<th>run</th>
<th>date (ymmd)</th>
<th>weight (g)</th>
<th>moist. content (wt %)</th>
<th>weight (g)</th>
<th>mois. content (wt %)</th>
<th>airflow rate (L/s, std)</th>
<th>reaction time (min)</th>
<th>ced carbon yield (%)</th>
<th>ABR delivered (kg/d)</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110726</td>
<td>1425.7</td>
<td>15.3</td>
<td>472.6</td>
<td>10.6</td>
<td>2.6</td>
<td>43.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>120215</td>
<td>1385.6</td>
<td>18.3</td>
<td>766.4</td>
<td>10.3</td>
<td>2.17</td>
<td>46.5</td>
<td>39.4</td>
<td>28.6</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>121026</td>
<td>2685.5</td>
<td>15.65</td>
<td>299.9</td>
<td>9.31</td>
<td>1.89</td>
<td>46.0</td>
<td>50.3</td>
<td>21.8</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>121114</td>
<td>1000.0</td>
<td>15.95</td>
<td>543.9</td>
<td>9.65</td>
<td>1.82</td>
<td>69.5</td>
<td>38.3</td>
<td>14.6</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>121120</td>
<td>1000.4</td>
<td>15.95</td>
<td>497.7</td>
<td>9.70</td>
<td>1.91</td>
<td>58.0</td>
<td>35.1</td>
<td>9.8</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>121221</td>
<td>1001.0</td>
<td>14.53</td>
<td>546.2</td>
<td>8.99</td>
<td>1.80</td>
<td>68.5</td>
<td>33.8</td>
<td>9.7</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>130124</td>
<td>1002.6</td>
<td>14.62</td>
<td>525.9</td>
<td>9.78</td>
<td>1.89</td>
<td>73.0</td>
<td>32.7</td>
<td>9.0</td>
<td>NA</td>
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<tr>
<td>8</td>
<td>130213</td>
<td>1000.08</td>
<td>14.64</td>
<td>478.3</td>
<td>8.45</td>
<td>1.79</td>
<td>66.0</td>
<td>36.2</td>
<td>16.3</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Wet basis. b Air-biomass (dry sewage sludge) ratio. Corncob ABR is constant at 1.11 kg/ha. c d char = mass dry char/mass dry feed. e dry ash free. f The dry weight of the wet sacrificial corncob on top of the sewage sludge bed. g In addition to corncob tinder on the bottom, the dry weight of the wet sacrificial corncob on top of the sewage sludge bed. *NA = not analyzed.

3. RESULTS AND DISCUSSION

The conditions and results of eight FC runs are summarized in Table S1 (see Supporting Information) displays the typical time—temperature behavior of S type K thermocouples located at various heights in the feedstock bed, as well as the reactor pressure, during a representative run. The biochar yield ($\chi_{\text{char}}$) and the fixed-carbon yield ($\chi_{\text{fc}}$) are defined in previous work1 from the University of Hawaii:

$$\chi_{\text{char}} = \frac{M_{\text{char}}}{M_{\text{feed}}}$$

where $M_{\text{char}}$ and $M_{\text{feed}}$ represent the dry masses of biochar and feedstock, respectively. The fixed-carbon yield incorporates the composition of the biochar:

$$\chi_{\text{fc}} = \chi_{\text{char}} \left( \frac{\%\text{C}}{100 - \%\text{feed ash}} \right)$$

where %C and %feed ash denote the percentage of fixed-carbon contained in the biochar and the percentage of ash in the feedstock, respectively. Of these runs, the first three were designed to identify favorable conditions for carbonization, whereas the remaining five employed virtually the same favorable conditions to study the reproducibility of the results.

The proximate analysis—originally developed to classify coals according to rank—offers key insights into the origin, production, and utility of the biochar. For example, some coals with low volatile matter (VM) content have been demonstrated to enhance the growth of plants when added to the soil.41 The ash content of the biochar also influences plant growth.42 Proximate analyses of the biochars produced in this work (excluding Run 1 which was not analyzed) are given in Table S1 (see Supporting Information). Reflecting the high ash content of the sewage sludge feed, only biochars with VM < 20% were accepted as fully carbonized. Run 3 failed to produce an acceptable biochar as the VM content of the top section exceeded 50%. A comparison of runs 7 and 8 reveals the sensitivity of the fixed-carbon yield to reaction conditions. Although the char yields are similar, the fixed carbon yield of run 8 is nearly double that of run 7. Table S1 shows that excessive air was delivered in Run 7 as evidenced by the very low VM content of its biochar (e.g., 1.7%) and its higher ash content.

The heavy-metal content of sewage sludge and its biochar can severely limit its use as a soil amendment. In the United

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Ghent University used a similar HNO3 microwave digestion method and HNO3/HCl digestion for Hg. TestAmerica Laboratories used EPA method 3050B40 (acid digestion by HNO3 and/or H2O2, with the digestion accelerated by microwave or hot plate up to 95 °C). As compared with EPA standard method 3010,40 which involves acid digestion by HNO3 and HCl, hot plate assisted up to 95 °C, Hazen Research used a more rigorous in-house method for acid digestion that might evoke higher values of heavy-metal concentrations. FQ Labs, TestAmerica Laboratories, and Ghent University reported heavy-metal concentrations on as-received bases, that were converted into dry bases concentrations. To accomplish these conversions, values of the moisture contents measured at the University of Hawaii were employed.

The condensates from Runs 4–8 were collected in two sumps (one at reactor pressure and one at atmospheric pressure) at the outlet of the reactor. These condensates were pooled, diluted with acetone to dissolve the tar present, and sent to three laboratories for analysis. FQ Labs, TestAmerica Laboratories, and Ghent University reported heavy-metal concentrations on as-received bases, that were converted into dry bases concentrations. To accomplish these conversions, values of the moisture contents measured at the University of Hawaii were employed.

As in our previous work, we employ a depletion ratio to quantify the loss of a heavy metal from material located in the canister:

$$\text{depletion ratio of element } i = 1 - \frac{M_{\text{char}} \times C_{\text{char},i}}{M_{\text{feed}} \times C_{\text{feed},i}}$$

where $C_{\text{feed},i}$ is the concentration (mg/kg) of the “ith” element in the feed, $C_{\text{char},i}$ is the concentration (mg/kg) of the “ith” element in the feed biochar, $M_{\text{char}}$ is the dry mass of the feed biochar (kg) in the canister, and $M_{\text{feed}}$ is the dry mass of the feed (kg) in the canister. Negative depletion ratios depict an uptake and absolute values greater than the amount taken up.

The corncob (CC) char uptake ratio measures the fractional uptake by corncob char of the loss of heavy metal from the sewage sludge (SS):

$$\text{uptake ratio of element } i = 1 - \frac{M_{\text{CC, char}} \times C_{\text{CC, char},i} - M_{\text{CC, feed}} \times C_{\text{CC, feed},i}}{M_{\text{S, feed}} \times C_{\text{S, feed},i}}$$

Due to budgetary constraints, corncob feed and biochar analyses were accomplished only for Runs 2 and 5. These data were employed to calculate the corncob biochar uptake ratio.
Table 4. Concentrations (mg/kg, dry) of Heavy Metals in the Raw Sewage Sludge and Sewage Sludge Biochars

<table>
<thead>
<tr>
<th>run</th>
<th>batch</th>
<th>lab</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Hg</th>
<th>Mo</th>
<th>Ni</th>
<th>Se</th>
<th>Zn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Raw Sewage Sludge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SS1</td>
<td>II</td>
<td>188</td>
<td>4.4</td>
<td>443</td>
<td>41</td>
<td>0.27</td>
<td>8.6</td>
<td>32</td>
<td>9.38</td>
<td>1360</td>
<td>67.6</td>
</tr>
<tr>
<td>2</td>
<td>SS2</td>
<td>II</td>
<td>6.79</td>
<td>3.3</td>
<td>325</td>
<td>13</td>
<td>0.53</td>
<td>11</td>
<td>30</td>
<td>8.58</td>
<td>956</td>
<td>97.4</td>
</tr>
<tr>
<td>5</td>
<td>SS3</td>
<td>IV</td>
<td>7.82</td>
<td>1.29</td>
<td>290</td>
<td>13.5</td>
<td>1.41</td>
<td>NA</td>
<td>21</td>
<td>6.7</td>
<td>855</td>
<td>46.9</td>
</tr>
<tr>
<td>6</td>
<td>SS3</td>
<td>II</td>
<td>4.66</td>
<td>3.2</td>
<td>346</td>
<td>14</td>
<td>0.28</td>
<td>9</td>
<td>27</td>
<td>8.58</td>
<td>1030</td>
<td>65.0</td>
</tr>
<tr>
<td>7</td>
<td>SS3</td>
<td>III</td>
<td>5.3</td>
<td>0.4</td>
<td>316.2</td>
<td>15.2</td>
<td>1.2</td>
<td>8.0</td>
<td>21.1</td>
<td>7.0</td>
<td>8199</td>
<td>42.2</td>
</tr>
<tr>
<td>8</td>
<td>SS3</td>
<td>I</td>
<td>6.4</td>
<td>0.4</td>
<td>407.6</td>
<td>5.9</td>
<td>0.5</td>
<td>10.5</td>
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<td>6.9</td>
<td>11280</td>
<td>49.5</td>
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<td></td>
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<td></td>
<td>Raw Corncob</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SS1</td>
<td>II</td>
<td>6.79</td>
<td>3.3</td>
<td>325</td>
<td>13</td>
<td>0.53</td>
<td>11</td>
<td>30</td>
<td>8.58</td>
<td>956</td>
<td>97.4</td>
</tr>
<tr>
<td>2</td>
<td>SS2</td>
<td>II</td>
<td>16.3</td>
<td>8.8</td>
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<td>2360</td>
<td>281</td>
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<td>II</td>
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<td>8.4</td>
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<td>2160</td>
<td>209</td>
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<td>IV</td>
<td>13.8</td>
<td>2.0</td>
<td>783</td>
<td>28.6</td>
<td>&lt;0.01</td>
<td>NA</td>
<td>635</td>
<td>12.0</td>
<td>2202</td>
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<td>SS3</td>
<td>II</td>
<td>7.66</td>
<td>9.1</td>
<td>1000</td>
<td>52</td>
<td>0.01</td>
<td>19.6</td>
<td>0</td>
<td>19.1</td>
<td>2940</td>
<td>178</td>
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<td>SS3</td>
<td>III</td>
<td>8.1</td>
<td>2.4</td>
<td>723.7</td>
<td>37.2</td>
<td>&lt;0.02</td>
<td>23.8</td>
<td>70.3</td>
<td>9.7</td>
<td>1964.4</td>
<td>113.7</td>
</tr>
<tr>
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<td>I</td>
<td>12.4</td>
<td>2.1</td>
<td>950.1</td>
<td>28.4</td>
<td>&lt;0.40</td>
<td>20.5</td>
<td>78.6</td>
<td>11.2</td>
<td>25622</td>
<td>112.0</td>
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</table>

Table 5. Historical Concentrations (mg/kg, dry) of Heavy Metals in Raw Sewage Sludge from the Hawaii Kai WWTP

<table>
<thead>
<tr>
<th>WWTP</th>
<th>year</th>
<th>As [mg/kg, dry]</th>
<th>Cd [mg/kg, dry]</th>
<th>Cu [mg/kg, dry]</th>
<th>Pb [mg/kg, dry]</th>
<th>Hg [mg/kg, dry]</th>
<th>Mo [mg/kg, dry]</th>
<th>Ni [mg/kg, dry]</th>
<th>Se [mg/kg, dry]</th>
<th>Zn [mg/kg, dry]</th>
<th>Cr [mg/kg, dry]</th>
</tr>
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<tbody>
<tr>
<td>Hawaii Kai</td>
<td>2010</td>
<td>1.83</td>
<td>0.50</td>
<td>73</td>
<td>4.12</td>
<td>NA [a]</td>
<td>NA [a]</td>
<td>5.11</td>
<td>1.00</td>
<td>200</td>
<td>12.1</td>
</tr>
<tr>
<td>(East Honolulu)</td>
<td>2011</td>
<td>1.77</td>
<td>0.611</td>
<td>120</td>
<td>4.82</td>
<td>NA [a]</td>
<td>NA [a]</td>
<td>12.40</td>
<td>5.80</td>
<td>350</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>2012</td>
<td>8.74</td>
<td>1.32</td>
<td>279</td>
<td>11.2</td>
<td>0.75</td>
<td>16.9</td>
<td>1</td>
<td>820</td>
<td>40.2</td>
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</table>

Table 6. Heavy Metal Regulations for Land Application of Sewage Sludge Biochar

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Hg</th>
<th>Mo</th>
<th>Ni</th>
<th>Se</th>
<th>Zn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA Ceiling conc[a] [mg/kg, dry]</td>
<td>75</td>
<td>85</td>
<td>4300</td>
<td>840</td>
<td>57</td>
<td>75</td>
<td>420</td>
<td>100</td>
<td>7500</td>
<td>NR</td>
</tr>
<tr>
<td>USA pollutant conc[a] [mg/kg, dry]</td>
<td>41</td>
<td>39</td>
<td>1500</td>
<td>300</td>
<td>17</td>
<td>75</td>
<td>420</td>
<td>100</td>
<td>2800</td>
<td>NR</td>
</tr>
<tr>
<td>USA load CPLR [kg/ha, dry]</td>
<td>41</td>
<td>39</td>
<td>1500</td>
<td>300</td>
<td>17</td>
<td>17</td>
<td>420</td>
<td>100</td>
<td>2800</td>
<td>NR</td>
</tr>
<tr>
<td>USA load APLR [kg/(ha·yr), dry]</td>
<td>2.0</td>
<td>1.9</td>
<td>75</td>
<td>15</td>
<td>0.85</td>
<td>D[b]</td>
<td>21</td>
<td>5.0</td>
<td>140</td>
<td>NR</td>
</tr>
<tr>
<td>State of Hawaii [mg/kg, dry]</td>
<td>20</td>
<td>15</td>
<td>1500</td>
<td>300</td>
<td>10</td>
<td>15</td>
<td>100</td>
<td>25</td>
<td>2000</td>
<td>200</td>
</tr>
<tr>
<td>Europe [mg/kg, dry]</td>
<td>20–40</td>
<td>1000–1750</td>
<td>750–1200</td>
<td>16–25</td>
<td>NR</td>
<td>300–400</td>
<td>NR</td>
<td>2500–4000</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>USA load [kg/(ha·yr), dry]</td>
<td>0.150</td>
<td>12</td>
<td>15</td>
<td>0.1</td>
<td>NR</td>
<td>3</td>
<td>NR</td>
<td>30</td>
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<tr>
<td>Belgium [mg/kg, dry]</td>
<td>150</td>
<td>6</td>
<td>375</td>
<td>300</td>
<td>5</td>
<td>NR</td>
<td>50</td>
<td>NR</td>
<td>900</td>
<td>250</td>
</tr>
</tbody>
</table>


States, both federal and state regulations define the legal limits of sewage sludge disposal on land, whereas in Europe both EU and individual country regulations are applicable. Some insight into this complex matrix of regulations is offered through the following discussion of the impacts of federal and Hawaiian, EU, and Belgian regulations concerning heavy metals on the legal addition of Hawaii Kai sewage sludge and its biochar to the soil.

As displayed in Table 4, we obtained heavy-metal analyses of the sewage sludge feed and its biochar from four different laboratories for each of the six runs summarized in Table 3. These data may be compared to annual averages of monthly analyses submitted to the U.S. EPA by the Hawaii Kai WWTP (see Table 5). Values listed in Table 5 for 2012 concur with those reported by FQ Labs and TestAmerica Laboratories for SS3 employed in our work (see Table 4). SS heavy-metal composition can vary greatly over time as shown by a study of different WWTPs on Oahu where the Zn concentration in SS was lower during certain months because of military inactivity. The concentrations of Cu, Ni, and Zn listed in Table 4 for the biochar are much higher than those reported by FQ Labs and TestAmerica Laboratories for different WWTPs on Oahu where the Zn concentration in SS was lower during certain months because of military inactivity.

Reference is due to the relatively low ash content of the HK SS and the consequent high weight loss incurred by pyrolysis (i.e., the concentrations of nonvolatile...
metals are magnified by the factor $1/y_{\text{char}}$. Note that Table 4 includes heavy-metal analyses of the raw corncob and corncob biochar from Runs 2 and 5. This data reveals the potential utility of corncob biochar as an adsorbent to reduce the amount of heavy metals carried by the gaseous effluent of the carbonization reactor.

In the United States, the land application of treated sewage sludge is governed by U.S. EPA regulation 40 CFR Part 503. If any of the heavy-metal ceiling concentrations in Table 6 is exceeded, the biochar cannot be applied to land. This is the first requirement governing land application. A review of the concentrations listed in Table 4 shows that none of the biochars produced in this work exceed the ceiling concentrations defined by the U.S. EPA. However, the Zn concentration of Run 6 (2940 mg/kg analyzed by Hazen Research) slightly exceeds the pollutant concentration limit (2800 mg/kg) listed in Table 6. Consequently, the addition of this biochar to the land is restricted by the U.S. EPA regulations. In this case, land application is allowed up to the cumulative pollutant loading rates (CPLR, in kg/ha) or the annual pollutant loading rates (APLR, in kg/(ha·yr)), as shown in Table 6. The APLR is the maximum amount of heavy metal that may be applied in one year for bagged solids and enables calculation of the annual whole sludge (biochar) application rate (AWSAR in t/ha with $t = \text{Mg}$) as follows:

$$\text{AWSAR} = \frac{\text{APLR}}{0.001C}$$

where $C$ is the concentration of heavy metal (mg/kg) and 0.001 is a conversion factor. The calculated APLR restrictions for the addition of Runs 5–8 biochar as bagged solids to the land are summarized in Table 7. The high concentration of Zn in this biochar limits its land addition to 48 t/(ha·yr). Recognizing the CPLR restriction of 2800 kg/ha for Zn, we see that Run 6 biochar can be applied to the land at a rate of 48 t/(ha·yr) for 20 years.

Note that different rules apply for bulk solids, and these are based upon the CPLR. Also, the land application of sewage sludge biochar, whose individual heavy-metal concentrations lie below their pollutant concentration limits, is not restricted. These biochars are designated to be “exceptional quality” by the U.S. EPA if they also meet class A pathogen reduction and vector control requirements (both of which are satisfied by carbonizing the sewage sludge).

According to the Hawaii Administrative Rules (see Table 6), the raw sewage sludge employed in Run 1 cannot be applied to land because of its high As concentration. All of the sewage sludge biochars exceed the state limits either for Ni, Zn, Mo, and/or Cr; hence none of the biochars produced in this work can be legally applied to the land in Hawaii.

According to EU law (see Table 6), all the Hawaii Kai sewage sludges and all their biochars (excepting Runs 6 and 5 due to their high Zn and Ni concentration, respectively) are acceptable for land application in the EU. Nevertheless, the EU limits the annual addition (in kg/(ha·yr) of sewage sludge biochar to the soil. The calculations for the maximum annual application rate in the EU are identical to the calculations for the AWSAR in the U.S. Table 7 lists the EU limits as calculated for each heavy metal using the laboratory analyses of Runs 6–8. The high concentrations of Zn and Cu in the biochars limit the application rate to 10–15 t/(ha·yr). Nickel limits the land application of SS biochar from Run 5 to 5 t/(ha·yr).

Finally, all of the sludges (excepting the feedstock of Runs 1 and 8) are compliant with Belgian regulations (see Table 6). However, irrespective of EU regulations, due to their high Cd, Cu, Ni, and Zn concentrations, none of the biochars listed in Table 4 can be applied to the land in Belgium. The addition of sewage sludge biochar to the soil may be feasible in other EU countries that have less stringent regulations than Belgium. We remark that this paper is among the few that compare heavy-metal concentrations not only to federal or European regulations but also to those imposed locally. We also note that despite U.S. EPA interest in total heavy-metal concentrations, the bioavailability of heavy metals in biochar is believed to be lower than that of raw sewage as applied to the land. Nevertheless wood biochar addition to soil has been shown to release heavy metals with negative effects on plant growth, and no general consensus exists. In addition to this, the high ash content of SS biochar could function as a base buffer that would prevent the release of heavy metals, but this phenomenon may be short-lived. The accumulation of heavy metal in plants depends upon the heavy metal, the plants, and soil conditions and results vary greatly.

To gain insight into the precision of the heavy-metal analyses, the condensates of Runs 4–8 were pooled, and a
single, well-mixed sample was sent to three certified laboratories for analysis (Hazen Research, TestAmerica Laboratories, and FQ Labs, see Table 8). We have used the results given in Table 8 to calculate the standard deviation associated with each concentration, which represents very preliminary experimental error estimates, and displayed these values as rough error intervals in Figure 1. In many cases (e.g., As, Cu, Ni, Se, Zn, and Cr), the analyses differ by “only” a factor of 2 or less, but in others the disagreement is much larger (e.g., Pb ranging from <0.46 to 15.19 mg/kg). We remark that analysis of the heavy metals requires their extraction by acid, and differences exist between the digestion methods employed by the laboratories. EPA method 3050B permits the addition of more HNO₃ to the sample if better recoveries of Ba, Pb, and Ag are required. This flexibility illustrates the dependency of the analysis on the operator. Likewise, Yafa and Farmer⁵⁵ mention the influence of different reagents, sample sizes, concentrations of reagents, and the volume of final product on the measured concentration of heavy metals. Comparison is difficult when different extraction techniques are used. Sequential extraction methods⁵⁶,⁵⁷ using different acids to remove heavy metals from sewage sludge reveal the effects of different species of the heavy metals on their leaching behavior. If the total amount of heavy metals is needed, a rigorous method employing HF is recommended (e.g., EPA method 3052).

Much can be learned about the release and migration of heavy metals from their depletion and uptake ratios. The depletion ratio measures the mass fraction of a heavy metal that leaves the feedstock during pyrolysis. Table 9 displays the depletion ratios for the heavy metals in order of their increasing boiling points. Negative values indicate an uptake by the sewage sludge biochar. We see that most of the Hg (81–99% with one outlier) and much of the As (30–96% with one outlier) in the sewage sludge is volatile. Arsenic is known to volatilize at temperatures as low as 200 °C depending on its chemical species and the presence of organic constituents.⁵⁸,⁵⁹ Similar depletion ratios for As were reported by Helsen et al.⁶⁰ Pressure is known to suppress the retention of As.⁶⁰ Mercury, and in lesser extents Se and As, are the only heavy metals leaving the reactor as aerosols or condensed on fine particles.⁶² Most of the other heavy metals are retained in the biochar. Apart from Hg, Zn, Pb, and Cu, the depletion ratios listed in Table 9 are lower than those measured for Ewa sludge in our laboratory.¹ Lienvens et al.⁶¹ reported depletion ratios up to 48% for Cd of Birch at 500 °C, similar to the depletion ratio in Run 5. The depletion ratios for Zn and Pb are consistent with the values given by van Lith et al.⁶⁴ for various woods at a pyrolysis temperature of about 500 °C. More generally, we note the difficulties associated with achieving good heavy-metal mass balances: Lienvens et al. mention uncertainties of 10–30% for heavy-metal mass balances even after recovering the heavy metals that adhered to the reactor walls.⁶²

The heavy-metal uptake ratios of the corn cob biochar at the bottom of the canister are especially interesting as they provide an indication of the ability of biochar to remove the volatile heavy metals released by the sewage sludge into the exhaust gas. We see in Table 9 that the corn cob biochar from Run 2 removes some of the Hg, Mo, and Ni from the pyrolysis gases, but is otherwise inert. Reflecting the scatter in measurements of Ni and Cr concentrations, corn cob biochar from Run 5 does not show the same behavior, but has negative uptake ratios for Ni and Cr that result from the high initial corn cob feed concentrations of these two metals. Kim et al. have reported similar findings, including the ability of biochar to readsorb arsenic during pyrolysis.⁵⁸ In our case, significant amounts of Hg, As, and Se leave the carbonizer in its gaseous effluents, whereas the heavy metals with high molecular weights (and high boiling points) remain with the sewage sludge biochar. Although these findings are in general agreement with our prior work, we emphasize that the behavior of the heavy metals is highly dependent upon their concentrations and speciation, Cl and S content, the oxygen partial pressure,⁵⁹,⁶²,⁶³,⁶⁵–⁶⁷ moisture⁶⁸,⁶⁹ and silica content, as well as the airflow rate, and reaction time employed during carbonization. Excessive depletion ratios tend to occur when heavy metals are highly volatile or strongly adsorbed to biochar. In our study, we report depletion ratios of 96% with one outlier)

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Concentrations (mg/kg) of heavy metals in the condensates with rough error intervals.

Table 9. Depletion and Uptake Ratios (g/g) with Heavy Metals Organized from Low to High Boiling Points

<table>
<thead>
<tr>
<th>ratio</th>
<th>run</th>
<th>lab</th>
<th>Hg</th>
<th>As</th>
<th>Se</th>
<th>Cd</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>depletion</td>
<td>1</td>
<td>II*</td>
<td>0.81</td>
<td>0.96</td>
<td>0.30</td>
<td>0.36</td>
<td>0.19</td>
<td>0.31</td>
<td>0.25</td>
<td>−0.20</td>
<td>−0.04</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>II</td>
<td>0.96</td>
<td>0.08</td>
<td>0.28</td>
<td>−0.03</td>
<td>0.07</td>
<td>0.00</td>
<td>0.07</td>
<td>0.01</td>
<td>0.06</td>
<td>−0.09</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>IV</td>
<td>1.00</td>
<td>0.32</td>
<td>0.31</td>
<td>0.41</td>
<td>0.01</td>
<td>0.19</td>
<td>−0.03</td>
<td>0.22</td>
<td>−11.0</td>
<td>NA⁶²</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>II</td>
<td>0.99</td>
<td>0.44</td>
<td>0.25</td>
<td>0.04</td>
<td>0.03</td>
<td>−0.26</td>
<td>0.02</td>
<td>0.07</td>
<td>0.12</td>
<td>0.26</td>
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<tr>
<td></td>
<td>7</td>
<td>III</td>
<td>0.99</td>
<td>0.50</td>
<td>0.55</td>
<td>0.34</td>
<td>0.22</td>
<td>0.20</td>
<td>0.25</td>
<td>0.12</td>
<td>−0.10</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>I</td>
<td>0.73</td>
<td>0.30</td>
<td>0.41</td>
<td>−0.90</td>
<td>0.18</td>
<td>−0.70</td>
<td>0.16</td>
<td>0.18</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>uptake⁶⁷</td>
<td>2</td>
<td>II</td>
<td>0.24</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>−0.03</td>
<td>0.01</td>
<td>0.00</td>
<td>0.08</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>IV</td>
<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>−0.68</td>
<td>−0.73</td>
<td>NA⁶²</td>
</tr>
</tbody>
</table>

*FQLabs, II = Hazen, III = TestAmerica, IV = Ugent. NA = not available. *Corn cob uptake ratio.
amounts of Cu, Cr, Zn, and As are reported to increase biochar yields.

4. CONCLUSIONS

(1) Most heavy metals with high boiling points (e.g., Pb, Ni, Cu, Zn, Cr) are largely retained in the biochar during carbonization, whereas Hg, and to a lesser extent As, Cd, and Se, are released during carbonization and leave the reactor. In the case of Mo, scatter in the analyses precludes a general rule.

(2) Biochar in the carbonizer does not adsorb significant quantities of the volatile heavy metals released during pyrolysis and cannot be employed to reduce emissions of these heavy metals from the carbonizer.

(3) Favorable fixed-carbon yields (e.g., 9.0−28.6%) can be realized at elevated pressure from sewage sludge, but this yield is sensitive to reaction conditions and control of the reactor.

(4) The challenging nature of heavy metal analysis is illustrated by the range of values obtained from three U.S. EPA accredited laboratories for the Pb content of a pyrolysis condensate: <0.46 mg/kg, 1.5 mg/kg, and 15.19 mg/kg. The range of values of Cd detected in the biochars (2.1−9.1 mg/kg) is also noteworthy. These disagreements are in part attributable to different digestion methods employed by the accredited laboratories and also reflect difficulties in controlling the carbonization procedure and obtaining reproducible results.

(5) Even on a small island, the heavy metal content of sewage sludge and its biochar vary greatly from one residential community to the next. Surprising variations are also observed in analyses of sludges from the same community from one year to the next.

(6) Due to their high content of the heavy metals Zn, Mo, and Cr, none of the biochars produced in this work from Hawaii Kai sewage sludge can be legally applied to the land in Hawaii. Likewise, due to the high levels of Cd, Cu, Ni, and Zn detected in these biochars, none can be legally applied to land in Belgium.

(7) Although a biochar may not be suitable for land application, it can still be mixed with coal and burned to generate power in a modern coal-fired facility equipped to capture heavy-metal emissions. Also, heavy-metal contaminated biochar can be used as an adsorbent for heavy metals as it has a high affinity for the most volatile heavy metal Hg and to lesser extents for As, Pb, Cu, Cd, and Cr. Another option is to reduce the heavy-metal concentration initially present in the sewage sludge by activated carbon, acids, or other techniques and utilize the heavy metals as a resource in the metal industry. Finally, we note that co-carbonization of sewage sludge with agricultural wastes may produce a biochar that can be legally applied as soil amendment. Certain biochars can reduce the bioavailability and phytotoxicity of heavy metals; consequently, the mixing of sewage sludge with agricultural wastes could potentially produce a biochar with beneficial effects.

ASSOCIATED CONTENT

Supporting Information

Carbonization temperature–time profiles at various positions in the feedstock bed, and proximate analyses of all the biochars described in this work. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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APPENDIX C
THE FUNDAMENTALS OF BIOCARBON FORMATION AT ELEVATED PRESSURE: FROM 1851 TO THE 21ST CENTURY
The fundamentals of biocarbon formation at elevated pressure: From 1851 to the 21st century

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Abstract

In 1851, Violette reported studies of wood carbonization in sealed glass tubes which endured considerable pressure at elevated temperatures and evoked unusual pyrolysis chemistry that led to very high charcoal yields. Despite the priority and promise of Violette’s work, his experiments were never reproduced and his findings forgotten. In this paper, we describe experiments that closely reproduce those of Violette and confirm many of his prescient observations. We employ small steel tubing bomb reactors rated to pressures above 13.9 MPa (2000 psig) at 400 °C that are heated quickly in a fluidized sand bath. Gas analysis is accomplished by an Agilent micro-GC and the charcoal product is subject to proximate analysis. Carbonization occurs at much lower temperatures than customary at atmospheric pressure. In the case of Avicel cellulose, the experimental fixed-carbon yield of charcoal exceeds the theoretical value derived from thermochemical equilibrium calculations. To the best of our knowledge, this is the first time that a pyrolysis process has produced a cellulosic char whose yield attained or exceeded its thermochemical equilibrium value.

1. Introduction

Due to increasing concern for climate change and rising sea levels, as well as tax incentives, the islands of Hawaii have witnessed exponential growth in the installation of photovoltaic (PV) panels during the past 5 years. For example, on the island of Maui the installed PV capacity doubled in 2011, 2012, and 2013. Similar growth is occurring worldwide, increasing the demand for silicon that is also a key ingredient in cellular phones, personal computers, televisions, and many other electronic marvels. Pure silicon is produced from quartz (SiO2) by use of a carbon reductant in an electric arc furnace that consumes large amounts of electric power. SiC is a necessary intermediate in the reduction process [1], and is formed at high temperatures in the arc furnace by the reaction:

\[
\text{SiO}(g) + 2\text{C}(s) \rightarrow \text{SiC}(s) + \text{CO}(g)
\]

Every silicon smelter in the world consumes either wood charcoal to provide carbon for the reduction reaction [1]. When wood is consumed, it undergoes pyrolysis in the arc furnace; thereby producing charcoal reactant for reduction reaction. Because wood charcoal is expensive, coal can be used as a supplementary reductant, but it is not preferred. Thus, we see that wood charcoal is a foundation stone of modern civilization.

Despite the fact that charcoal has been manufactured by man for more than 30,000 years, its production is inefficient (i.e., the yield of charcoal is low), and is a significant source of pollution in developing countries [2]. Improving the charcoal yield is the principal objective of this paper. The maximum charcoal yield can be estimated by a thermochemical equilibrium calculation that predicts the amount of carbon produced from wood pyrolysis at a given temperature and pressure [2–7]. Throughout this paper we use cellulose as a model compound for wood. Thermochemical equilibrium calculations for cellulose indicate a maximum carbon yield of 28 wt% over a wide range of pressures at temperatures near 400 °C [4,8].

But charcoal is not pure carbon. The silicon industry purchases charcoal on the basis of its fixed-carbon content (% fC) that measures its effectiveness as a reductant. In view of the silicon industry’s emphasis of fixed-carbon, together with the fact that fixed carbon is nearly pure carbon, we define the fixed-carbon yield of a pyrolysis process as \(y_{fC} = \frac{y_{\text{char}}}{(\% \text{ feed ash})} \times \% \text{ feed ash} \), where \(y_{\text{char}} = \frac{M_{\text{char}}}{M_{\text{bio}}} \); \(M_{\text{char}} \) and \(M_{\text{bio}} \) are the dry masses of the charcoal and wood feedstock (respectively), and % feed ash is the ash content of the dry feedstock [3,4,6,7].
During the past 15 years we have studied the influences of composition, particle size, and pressure on the fixed-carbon yield of various biomass feedstocks, and compared the measured experimental values of the fixed-carbon yield with the calculated thermochemical equilibrium value. Excepting a few cases, the measured fixed-carbon yield varied between <40% to ~80% of the theoretical equilibrium value [6,7]. The highest yields were obtained with flowing air at elevated pressure (~1 MPa) in a Flash Carbonization reactor [4,5,9]. Reproducible fixed-carbon yields above ~80% of the theoretical value have not been achieved. The goal of this paper is to identify reaction conditions that realize the theoretical thermochemical equilibrium value of the fixed-carbon yield.

Thermogravimetric analyses of cellulose reveal the extreme difficulty in achieving high fixed-carbon yields of charcoal from pure cellulose. For example, the round-robin study described by Gronli et al. realized char yields of 3.3 wt% from a 0.94 mg sample of Avicel cellulose heated to 400 °C in flowing nitrogen that fell to 2.2 wt% for a 0.11 mg sample [10]. Some researchers believe that the char yield from pure cellulose approaches zero as the sample size approaches zero [11]. Because cellulose represents an extreme case of difficulty in realizing high fixed-carbon yields, we emphasize cellulose pyrolysis throughout the remainder of this paper.

Although pressure is predicted by thermochemical equilibrium calculations to have a negligible effect on carbon yields from cellulose [4], experiments tell a different story. Using a tubular pressure vessel within a differential scanning calorimeter, thirty years ago Mok and Antal showed that elevated pressures greatly augment the char yield (and presumably the fixed-carbon yield) from cellulose [12–14]. Also, the flow rate of gas over the solid cellulose sample affected the char yield; lower flows considerably increased the char yield. Taken together, an increase in pressure from 0.1 to 2.5 MPa with a low flow of sweep gas increased the char yield from 10 wt% to 22 wt% at 500 °C. These findings suggest that maximum fixed-carbon yields can be obtained by pyrolysis in a closed vessel at elevated pressure without gas flow.

In 1851, Violette reported astounding studies of wood pyrolysis in sealed glass vessels that developed high pressures due to increased temperatures and gas evolution during pyrolysis [15]. The following are highlights of his research:

1. Dry wood (1 g) was carbonized from “150” to “350” °C in sealed glass tubes (4 at each temperature with little void volume).
2. Each tube was held in a metal safety container because carbonization created “enormous” gas pressures.
3. Violette reported a value of $y\text{char} = 78.7\%$ at 320 °C with $%C = 65.6\%$ (vs. $y\text{char} = 29.7\%$ at 0.1 MPa)!
4. Charcoal at 180 °C was said to resemble ordinary “red” charcoal at 280 °C.
5. Charcoal at 300 °C was said to resemble coking coal having undergone melting: glossy, shiny, brittle and bonded to the glass tube.
6. Violette measured ash contents of 3–4% vs. 0.5% with ordinary charcoal.
7. Also a milky opaque white or (sometimes) clear yellow liquid product was detected.

Violette’s prescient research has been largely forgotten, perhaps because the temperature scale was not well defined in the 1850’s. For example, Violette believed that antimony melted at 432 °C; whereas, its true melting point is 631 °C. Consequently, many of the temperatures mentioned in Violette’s papers are underestimates of the true temperature. Nevertheless, the extraordinary yields of carbon reported by Violette confirm our hypothesis that pyrolysis in sealed vessels holds promise for improving the fixed-carbon yields of charcoal from wood.

To the best of our knowledge, the only other work involving pyrolysis in sealed vessels was reported by Mok et al. in 1992 [16]. The following are highlights of their paper:

1. At high loadings charcoal formation from cellulose is complete below 300 °C.
2. The reaction rate is greatly enhanced in a closed crucible.
3. The reaction rate and char yield is greatly enhanced by high moisture content.
4. Pyrolysis is exothermic for all cases.

Five years later Varheggi et al. described a kinetic model, which included reactions representing the catalytic action of water on charcoal yields that well fit the differential scanning calorimetry data of Mok et al. [17,18]. Unfortunately, Violette and Mok et al. did not measure fixed-carbon yields, and other questions, such as the yield of tar and gas, remain unanswered. In this paper we describe preliminary studies of Avicel cellulose pyrolysis in sealed tubing bombs with emphasis of measured fixed-carbon yields and their comparison with the theoretical value. As mentioned above, char yields from pure, crystalline cellulose (e.g., Avicel) at atmospheric pressure are notoriously low. Our goal is to attain the theoretical fixed-carbon yield of charcoal from cellulose (i.e. $y_c = 28$ wt%). Conditions which realize the theoretical fixed-carbon yield of charcoal from cellulose are likely to offer very high fixed-carbon yields of wood charcoal as well.

2. Methods

2.1. Apparatus

The apparatus (see Fig. 1) is separated into sections. The tubing bomb is constructed of 1” stainless steel tubing (rated 3100 psig, 37 °C with Swagelok fittings. Each section volume was calibrated by pressurizing the required sections with air from a calibrated cylinder (i.e., “air cart”), with the air cart pressure ($P_1$) and the pressure transducer ($P_2$) recorded. The air was then transferred to a custom glass water displacement vessel (WDV) (3 L), with the displaced water weighed and the measurement converted to volume. The apparatus as a whole ($V_\text{bomb}$) has an empty volume of 0.098 L; the estimated inert volume ($V_I$) of gas that is assumed to not take part in the reaction is 0.056 L, while the active volume ($V_A$) that does participate in pyrolysis is 0.067 L when empty.

2.2. Procedure

Each piece of the tubing bomb was weighed individually before the bomb was loaded with microcrystalline cellulose (Avicel, Lot# 2324, Type PH 102, FMC bioPolymer). The ash content of Avicel is specified by its manufacturer as <0.05 wt%. We employed ASTM D3516-89 (2011) to determine the ash content of the Avicel fed to our reactors, and confirmed its ash content to be 0.044 wt% by a triplicate measurement. The manufacturer specifies its particle size distribution as follows: 10 wt% <15–55 μm, 50 wt% <80–140 μm, 90 wt% <170–283 μm. The annular volume between the outer wall of the thermocouple well and the inner wall of the tubing bomb was filled to the top with charcoal. Weighed glass wool was positioned on top of the cellulose to prevent the cellulose powder from being displaced during gas filling.

The initial filled volume of the tubing bomb was found by pressurizing (∼3) the bomb with air from the air cart. By use of the calibrated volume of the air cart and the pressure changes recorded at $P_1$ and $P_2$ during the filling we calculated the initial void volume of the filled vessel.
The tubing bomb was vacuumed, purged, and pressurized to 100 psig with nitrogen or oxygen in preparation for an experiment. During vacuuming and purging $V_5$ (see Fig. 1) was closed to protect the pressure transducer and burst diaphragm, and was opened when refilling.

The experiment was begun when the pressurized tubing bomb was lowered into a preheated fluidized sand bath (300 °C). The tubing bomb axis temperature, its outer wall temperature, and pressure ($P_2$), along with the sand bath temperature were recorded (10 s intervals) for the duration of the experiment using LabView (National Instruments). The experiment was concluded when the outer wall and axis temperature differed by $5$ °C after the observation of an exotherm or when the pressure became steady. To end the experiment the tubing bomb was raised from the sand bath. Cooling was accelerated using an electric fan. Once cooled to room temperature, the apparatus was prepared for removal of both the pyrolysis solid and gas product.

2.3. Pyrolysis gas product

The gas was transferred from the tubing bomb to the WDV. Using Eq. (2) this volume can be used to find the final volume of the tubing bomb after pyrolysis (see Table 1).

$$P_2(V_{bomb} + V_{SV}) = P_{Lab}(V_{WDV} + V_{bomb} + V_{SV})$$

A sample needle (with a glass wool and Drierite filter) connected to the rear injection port of a 490 Micro GC (Agilent Technologies) was used to sample gas from the WDV. He carrier gas (Airgas) was used on both columns along with 80 ms injection times. The gases Ne, H$_2$, O$_2$, N$_2$, CH$_4$, and CO were detected using a 10 m

---

**Table 1**
The variable gas volumes used in the tubing bomb apparatus for each experiment.

<table>
<thead>
<tr>
<th>Term</th>
<th>Measured</th>
<th>$O_2$ (2.28 MPa)</th>
<th>$N_2$ (2.26 MPa)</th>
<th>$N_2$ (0.10 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubing bomb gas volume [$V_{bomb}$]$^a$</td>
<td>Initial: AC</td>
<td>0.082</td>
<td>0.085</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>Final: WDV</td>
<td>0.097</td>
<td>0.090</td>
<td>0.095</td>
</tr>
<tr>
<td>Void volume [$V_{void}$]$^b$</td>
<td>Initial: AC</td>
<td>0.019</td>
<td>0.022</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>Final: WDV</td>
<td>0.034</td>
<td>0.027</td>
<td>0.032</td>
</tr>
<tr>
<td>Active volume [$V_A$]$^c$</td>
<td>Initial: AC</td>
<td>0.051</td>
<td>0.054</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>Final: WDV</td>
<td>0.066</td>
<td>0.059</td>
<td>0.064</td>
</tr>
</tbody>
</table>

$^a$ The gas volume of the tubing bomb plus dead volume ($V_{DV} + V_{ADV} + V_{void}$).

$^b$ The volume of gas that occupies the empty space in the packed bed of feed and takes part in the chemistry of the reaction.

$^c$ The sum total of the active dead volume and void volume.

$^d$ AC defines volume measurements made using the pressure difference recorded using an air cart. WDV defines volume measurements made using a water displacement vessel.
Molsieve 5 Å column (Backflush 11 s, Pressure 30 psi, Column Temperature 80 °C). CO2 was detected with a 10 m PolarPlotU column (Backflush 17 s, Pressure 25 psi, Column Temperature 60 °C). Calibration curves were constructed using injection times 10 ms, 20 ms, 40 ms, 80 ms, 160 ms, 240 ms with room air and calibration gases GMT10403TG, GMT10406TG (Matheson Tri-Gas Inc.). The data was processed using Excel (Microsoft). Mol balances of 100% ± 5% were obtained for the experimental gas samples, with replicate (∼×4) reproducibility being greater than 95%.

2.4. Pyrolysis Solid Product

Once the gas product was sampled, the tubing bomb was removed from the rest of the apparatus to facilitate removal of the solid product.

The tubing bomb was disassembled and weighed in an order reverse of the feed loading. The charcoal product was weighed and collected for proximate analysis. The final product weight was regarded to be the amount collected. Some product was lost during removal of the product from the tubing bomb. A moisture content analysis was done on the glass wool.

Moisture content analyses for the reactant cellulose and product glass wool were performed according a modified version of ASTM 1756-08. The most significant differences were that the sample mass was decreased to a minimum of 0.5 g and the initial drying time was decreased to 2 h. Proximate analysis of the product charcoal was determined according to ASTM D1762-84.

3. Results and discussion

Fig. 2 displays the measured wall and axis temperatures of the tubing bomb, and its internal pressure during experiments conducted under nitrogen initially at 0.10 MPa, and with oxygen initially at 2.28 MPa and nitrogen initially at 2.26 MPa. At first the axis temperature lags the wall temperature (as expected). In the case of the atmospheric pressure experiment, the sudden rise of the axis temperature above the wall temperature plainly evidences the strong exotherm associated with carbon formation from cellulose. This rise is associated with a leap in pressure due to gas release during pyrolysis. Although the axis temperature does not exceed the wall temperature in the 2.26 MPa nitrogen experiment, the axis heating rate is high and the pressure rise is greatly enhanced. Finally, under oxygen both the temperature rise and pressure rise are exceedingly sharp.

Table 2 lists the reaction conditions and results of the 3 experiments. Apart from gas loading, the experiments employed similar conditions. The 2 experiments conducted at elevated initial pressure reached much higher peak pressures than the experiment initially at atmospheric pressure (i.e. 7–8 MPa vs. 1.7 MPa). The increase in Vb, during each run was due to the shrinkage of the solid resulting from its mass loss.

As expected from previous work, values of ychar (47.2–56.5 wt%) are remarkably high. These findings corroborate those of Violette [15]. Unfortunately, these values are also meaningless as they do not reflect the quality (e.g. fixed-carbon content) of the char. Nevertheless, in this case the high values of ychar accurately hint of the high values of yfC realized in these experiments: yfC = 26.7–34.0 wt%; the highest value resulting from pyrolysis under pure nitrogen at 2.26 MPa, and the lowest representing pyrolysis under pure oxygen at 2.28 MPa. Both experiments under nitrogen realize fixed-carbon yields that exceed the theoretical “limit” given by thermodynamics (i.e. 28 wt%), and even the experiment under oxygen attains this limit within the margin of error associated with the measurements. We note that these charcoals are not suitable for metallurgical applications as their VM content is too high. The VM content is high because the heat treatment temperature (HTT) was restricted to 300 °C in this preliminary work due to concerns for the safety of the equipment at high pressures and temperatures. Recent findings, which we will report in the near future, have substantiated the very high fixed-carbon yields listed in Table 2, together with lower VM contents. At 400 °C we have obtained fixed-carbon yields well above 32 wt% with VM contents as low as 25 wt%.

Increasing the overpressure of nitrogen from 0.1 MPa to 2.26 MPa favors the pyrolytic formation of CO2, and has little effect on the formation of CO. The yields of H2 and CH4 are very small. As expected, the yields of CO2 and CO are greatly enhanced by pyrolysis under oxygen. Surprisingly, the yields of H2 and CH4 are also enhanced. These values may be compared with those reported by Antal [19] for pyrolysis of cellulose under flowing steam at 0.1 MPa (i.e., constant pressure). The constant pressure flow reactor yield of CO2 (6 wt%) was very similar to the constant volume tubing bomb value (6.45 wt%) at 0.1 MPa, but the yield of CO at constant pressure (4 wt%) was much higher. Furthermore, increasing the initial N2 pressure of the tubing bomb to 2.26 MPa increased the yield of CO2 (i.e., 9.98 wt%) relative to the constant pressure value (i.e., 6 wt%), without significantly changing the other gas yields. Enhanced formation of CO2 at elevated pressure in the tubing bomb is indicative of the efficient removal of oxygen during the formation of solid carbon product and is associated with high values of yfC.

Recall that the ash content of the Avicel was determined to be 0.044 wt% by a triplicate measurement. In view of this determination, the ash contents of the cellulose chars are inexplicably high. These anomalously high values corroborate the observations of Violette [15] regarding the enhanced ash contents of the wood chars produced in his sealed vessels. More work is needed to confirm the composition and origin of this ash product.

We have not displayed photographs of the char product because these photos do not capture the true, fascinating appearance of the solid carbon residue. The char product of the 0.1 MPa N2 experiment did not pass through a liquid phase. The top half of the char crumbled into a powder with similar texture to Avicel as it was spooned out of the tubing bomb. The bottom half was not caked and poured out of the reactor like a dry powder. All the char was dark black with hints of brown. These results are unlike those of Violette [15]. On the other hand, much of the char product of the 2.26 MPa N2 experiment passed through a liquid phase. The carbon near the axis was deep black, fused, brittle, glittery, and had a bubbly inner surface. The carbon near the outer wall had a grainy, crunchy texture. Violette’s description of his charcoals [15] is apt in describing our 2.26 MPa N2 charcoal. We note that Violette had
Table 2
Comparing the parameters and results for cellulose pyrolysis when under O$_2$ (2.28 MPa), N$_2$ (2.26 MPa) and N$_2$ (0.10 MPa) and heated to 300 °C.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>O$_2$ (2.28 MPa)</th>
<th>N$_2$ (2.26 MPa)</th>
<th>N$_2$ (0.10 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid feed moist mass [g]</td>
<td>16.95</td>
<td>16.77</td>
<td>15.90</td>
</tr>
<tr>
<td>Solid feed moisture content [%]</td>
<td>5.44</td>
<td>4.72</td>
<td>4.74</td>
</tr>
<tr>
<td>Gas contained in VBomb + VSV [mol]</td>
<td>0.1040</td>
<td>0.1064</td>
<td>0.0045</td>
</tr>
<tr>
<td>Pyrolysis Reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean HTT [°C]</td>
<td>299</td>
<td>309</td>
<td>291</td>
</tr>
<tr>
<td>Axis peak temperature [°C]</td>
<td>335</td>
<td>305</td>
<td>332</td>
</tr>
<tr>
<td>Wall Peak Temperature [°C]</td>
<td>306</td>
<td>305</td>
<td>287</td>
</tr>
<tr>
<td>Peak pressure [MPa]</td>
<td>8.18</td>
<td>7.39</td>
<td>1.68</td>
</tr>
<tr>
<td>VBomb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.082</td>
<td>0.085</td>
<td>0.081</td>
</tr>
<tr>
<td>Final</td>
<td>0.097</td>
<td>0.090</td>
<td>0.095</td>
</tr>
<tr>
<td>Solid Products</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final solid product moist mass [g]</td>
<td>9.88</td>
<td>11.82</td>
<td>9.72</td>
</tr>
<tr>
<td>Final moisture content [%]</td>
<td>23.9</td>
<td>24.3</td>
<td>18.0</td>
</tr>
<tr>
<td>Final solid product dry mass + volatile matter on glass wool [g]</td>
<td>7.56</td>
<td>9.03</td>
<td>7.87</td>
</tr>
<tr>
<td>Percentage dry mass change [%]</td>
<td>52.8</td>
<td>43.5</td>
<td>48.1</td>
</tr>
<tr>
<td>Volatile matter content [%]</td>
<td>38.8</td>
<td>39.0</td>
<td>48.5</td>
</tr>
<tr>
<td>Ash content [%]</td>
<td>0.3</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Fixed carbon content [%]</td>
<td>60.9</td>
<td>60.1</td>
<td>51.5</td>
</tr>
<tr>
<td>Fixed carbon yield [%]</td>
<td>28.7</td>
<td>34.0</td>
<td>26.7</td>
</tr>
<tr>
<td>Gas Products</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final gas in VBomb + VSV [mol]</td>
<td>0.178</td>
<td>0.152</td>
<td>0.036</td>
</tr>
<tr>
<td>Nitrogen [mol%]</td>
<td>0.00</td>
<td>74.30</td>
<td>17.67</td>
</tr>
<tr>
<td>Oxygen [mol%]</td>
<td>39.23</td>
<td>0.82</td>
<td>0.11</td>
</tr>
<tr>
<td>Hydrogen [g/g (Dry Feed)]</td>
<td>0.00052</td>
<td>0.00004</td>
<td>0.00002</td>
</tr>
<tr>
<td>Methane [g/g (Dry Feed)]</td>
<td>0.00261</td>
<td>0.00007</td>
<td>0.00010</td>
</tr>
<tr>
<td>Carbon Monoxide [g/g (Dry Feed)]</td>
<td>0.06416</td>
<td>0.01666</td>
<td>0.01555</td>
</tr>
<tr>
<td>Carbon Dioxide [g/g (Dry Feed)]</td>
<td>0.16942</td>
<td>0.09975</td>
<td>0.06451</td>
</tr>
<tr>
<td>Mass Balance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas products [wt%]</td>
<td>23.67</td>
<td>11.65</td>
<td>8.02</td>
</tr>
<tr>
<td>Charcoal Yield [wt%]</td>
<td>47.19</td>
<td>56.51</td>
<td>51.95</td>
</tr>
<tr>
<td>Water + Water on Glass Wool [wt%]</td>
<td>13.56</td>
<td>22.40</td>
<td>19.22</td>
</tr>
<tr>
<td>Total</td>
<td>84.42</td>
<td>90.56</td>
<td>79.18</td>
</tr>
</tbody>
</table>

virtually no dead volume in his sealed glass tubes, whereas our tubing bombs have excess dead volume related to plumbing for the pressure transducer, the thermocouple leads, and the burst diaphragm. Consequently, Violette’s experiments must have developed much higher pressures than we obtained at 0.1 MPa, and this may explain why his charcoals resembled our 2.26 MPa N$_2$ charcoal. The charcoal produced under oxygen at 2.28 MPa resembled the 2.26 MPa N$_2$ charcoal.

The mass balances of the three experiments, ranging from 79.2 to 90.6 wt% are somewhat disappointing. We believe the deficit primarily reflects difficulties in collecting and weighing water formed during the experiment, which condenses throughout the apparatus and is difficult to collect, as well as the difficulty in collecting the carbon product. Little tar is formed and its quantification is quite difficult.

The role of pressure in directing the underlying pyrolysis chemistry towards the formation of fixed carbon can be understood in light of the complementary findings of many brilliant researchers during the past 50 years. A detailed review of this prior work is beyond the scope of our paper, but will be offered in the near future. Here we offer a terse summary of the highlights. In the late 1960’s and 1970’s Broido, Arseneau, Shafizadeh and co-workers identified the role of competing reactions during cellulose pyrolysis in the formation of either monomeric levoglucosan (depolymerization reactions) vs. char (condensation reactions). Their pioneering work is summarized in the reviews of Antal, [20,21]. In the 1980’s Diebold, Reed, Lédé, Scott and coworkers discovered and exploited the utility of rapid heating (“flash” or “fast” pyrolysis) in driving the depolymerization reactions and thereby favoring the formation of oligomers and “intermediate liquid compounds (ILC)”. Lédé offers a detailed and insightful discussion of this seminal work in his review [22]. Very recently, Bai, Brown and co-workers confirmed that levoglucosan (the ILC) passes through a liquid phase on its way to becoming a vapor [23–25]. In the case of cellulose, the vapor can be condensed to obtain high yields of monomer levoglucosan. The discovery by Scott, Piskorz, Radlein and their co-workers of glycolaldehyde as a significant byproduct of cellulose fast pyrolysis, and the mechanism of this commercially important reaction as detailed by Richards and his co-workers, are reviewed by Antal and Varhegyi [11]. The heat of vaporization of levoglucosan and its vapor pressure have been reported by Milosavljevic, Oja and Suuberg [26,27], and Rocha et al. [28] Their findings indicate that the vapor pressure of levoglucosan greatly exceeds 0.1 MPa at pyrolysis temperatures; consequently it boils vigorously during pyrolysis at 0.1 MPa and its rate of mass transfer to the vapor phase is high. All these findings taken together unveil the role of pressure in directing the pyrolysis reactions towards the formation of carbon. As first described by Mok and Antal, [12–14], and later corroborated by Hajaligol, et al. [29], Milosavljevic et al. [26], Rath et al. [30], Gomez et al. [31], Rouset et al. [32] and others, when the external pressure exceeds the vapor pressure of the liquid intermediate, the intermediate does not boil and its rate of mass transfer to the vapor phase is slow. Consequently, the liquid phase persists. Condensation reactions are favored in the liquid phase, and these reactions are responsible for the high fixed-carbon yields reported in this paper. When the external pressure does not exceed the vapor pressure of the liquid intermediate, but is nevertheless elevated, the specific volume of the vapor is reduced; consequently it is retained longer in the pores of the solid undergoing pyrolysis and has greater opportunity to experience secondary heterogeneous reactions that lead to carbon formation [33,34].

4. Conclusions

1. With >32,000 years of experience, we now understand the conditions needed to realize the theoretical fixed-carbon yield of charcoal from ash-free cellulose. These conditions involve pyrolysis in a sealed vessel that reaches pressures exceeding 1.68 MPa.
2. In 1853, Violette reported remarkably prescient research concerning charcoal production in sealed vessels (but he did not measure the fixed-carbon yield). In this paper we corroborate his observations.

3. In addition to Violette’s observation of very high charcoal yields obtained from pyrolysis in sealed vessels, we also confirm his observation of anomalously high ash yields and the role of a molten phase in charcoal formation at high pressures.

4. Also we note that elevated pressures in sealed vessels enhance the yield of CO2 without affecting the CO yield. The yields of H2 and CH4 are negligible. The enhanced yield of CO2 is a signature of selective pyrolysis chemistry associated with enhanced fixed-carbon yields.

5. The observation of a liquid phase when charcoal is formed with high fixed-carbon yields links high pressure pyrolysis chemistry to high heating rate pyrolysis chemistry.

6. Numerical simulations of sealed vessel results (e.g., pressure, temperature gradients, gas and char fixed-carbon and volatile matter compositions) promise to reveal much about the mechanism of cellulose pyrolysis.

7. In view of the remarkable work of Violette, the following advice to young researchers is apropos:

   A year of long days, late evenings and weekends in the laboratory will save you an afternoon of reading interesting papers in the library.

Acknowledgment

We acknowledge support by the National Science Foundation (Award CBET11-58965), the Office of Naval Research under the Hawaii Energy and Environmental Technologies (HEET) initiative, and the Coral Industries Endowment of the University of Hawaii Foundation. We thank Ms. Bonnie Thompson, Dr. Sumanta Acharya, and Dr. Sohi Rastegar (all of NSF) for their continuing interest in biochars, Lloyd Paredes, Kathryn Hu and Maider Legarra (UH) for assistance with the experiments. The corresponding author (MJA) thanks Prof. Dr. Colomba Di Blasi of the Università degli Studi di Napoli “Federico II for hosting a three week visit to her laboratory during which she encouraged further research on the topics of this paper at UH.

References

APPENDIX D
TEMPERATURE AND PRESSURE HISTORIES OF LAB-SCALE EXPERIMENTS USING NORWEGIAN WOOD

Figure D.1. Temperature and pressure history of the February 12 2015 Lab-scale experiment.

Figure D.2. Temperature and pressure history of the February 19 2015 Lab-scale experiment.
APPENDIX E
TEMPERATURE AND PRESSURE HISTORIES OF DEMO-SCALE EXPERIMENTS USING MACADAMIA NUT SHELL

Figure E.1. Overview of the temperature/pressure/oxygen concentrations during the FC demo experiment done on January 27, 2014.

Figure E.2. Overview of the temperature/pressure/oxygen concentrations during the FC demo experiment done on March 4, 2014.
Figure E.3. Overview of the temperature/pressure/oxygen concentrations during the FC demo experiment done on April 14, 2014.
APPENDIX F
DRAWING NEW METERING DISC FOR BONNEY FORGE
HL-31 GLOBE VALVE
In this appendix 1-13 the input and output of Stanjan are shown below.

**Number 1:** Cowboy Oak sawdust at constant pressure with elemental N

**Number 2:** Cellulose at constant pressure with elemental N

**Number 3-7:** Cellulose at different packing densities with N\(_2\) and elemental N

**Number 8:** Cellulose at constant pressure without N\(_2\) and without elemental N

**Number 9-12:** Cellulose at different packing densities without N\(_2\) and without elemental N

**Number 13:** Cellulose at constant pressure with elemental N and N\(_2\)

---

### Appendix 1. Cowboy Oak Wood at Constant Pressure P =10 atm (N in elemental)

#### INPUT

**Computed properties**

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.30300000E-01</td>
</tr>
<tr>
<td>H</td>
<td>4.69600000E-01</td>
</tr>
<tr>
<td>O</td>
<td>1.99400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>8.00000000E-04</td>
</tr>
</tbody>
</table>

Reactants at P = 1.000E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.33027E+00</td>
<td>.33027E+00</td>
<td>.51912E+00</td>
<td>3.30300E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46955E+00</td>
<td>.46955E+00</td>
<td>.61938E+00</td>
<td>4.69600E-01</td>
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<tr>
<td>N</td>
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<td>.79992E-03</td>
<td>.14664E-02</td>
<td>8.00000E-04</td>
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<tr>
<td>O</td>
<td>.19938E+00</td>
<td>.19938E+00</td>
<td>.41747E+00</td>
<td>1.99400E-01</td>
</tr>
</tbody>
</table>

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

#### Mixture properties:

<table>
<thead>
<tr>
<th>molal mass = 7.641 kg/kmol</th>
<th>T = 298.00 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 1.0133E+06 Pa</td>
<td>V = 3.2000E-01 m**3/kg</td>
</tr>
<tr>
<td>U = 5.0525E+07 J/kg</td>
<td>H = 5.0849E+07 J/kg</td>
</tr>
<tr>
<td>S = 1.6720E+04 J/kg-K</td>
<td></td>
</tr>
</tbody>
</table>

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

---

### OUTPUT
Computed properties

Independent population element atom potential
C  3.30300000E-01  -1.0513
H  4.69600000E-01  -8.7665
O  1.99400000E-01  -47.8088
N  8.00000000E-04   34.3547

Products at T = 673.00 K     P = 1.000E+01 atmospheres

species     mol fraction    mol fraction    mass fraction      mols* in the phase in mixture in mixture

phase 1: molal mass = 21.863 kg/kmol
CH4         .25167E+00     .12304E+00     .11730E+00     5.58776E-02
CO          .11862E-02     .57993E-03     .96533E-03     2.63373E-04
CO2         .18934E+00     .92566E-01     .24209E+00     4.20383E-02
H2          .39567E-01     .19344E-01     .23174E-02     8.78480E-03
H2O         .51463E+00     .25159E+00     .26936E+00     1.14260E-01
NO          .36032E-02     .17616E-02     .31413E-02     8.00000E-04
NO2         .79217E-17     .38728E-17     .10589E-16     1.75881E-18

phase 2: molal mass = 12.011 kg/kmol
C(S)        .10000E+01     .51112E+00     36482E+00     2.32121E-01

phase 3: molal mass = .000 kg/kmol
H2O(L)      .00000E+00     .00000E+00     .00000E+00     0.00000E+00

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 16.828 kg/kmol
T = 673.00 K     P = 1.0133E+06 Pa     V = 1.6057E-01 m**3/kg
U =-5.8989E+06 J/kg     H =-5.7362E+06 J/kg     S = 6.6749E+03 J/kg-K

Made 0 (T,P) iterations; 15 equilibrium iterations; v 3.91 IBM-PC
**Appendix 2. Cellulose at Constant Pressure P = 680 psig ≈ 47 atm (N in elemental)**

**INPUT**

Computed properties

<table>
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<tr>
<th>atoms</th>
<th>population</th>
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</thead>
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<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>1.37000000E-04</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
</tr>
<tr>
<td>phase 1: molal mass = 7.865 kg/kmol</td>
<td>T = 298.00 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.29096E+00</td>
<td>.44432E+00</td>
<td>7.11743E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.46518E+00</td>
<td>.59615E-01</td>
<td>1.13793E+00</td>
</tr>
<tr>
<td>N</td>
<td>.56005E-04</td>
<td>.56005E-04</td>
<td>.99745E-04</td>
<td>1.37000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.24381E+00</td>
<td>.49597E+00</td>
<td>5.96400E-01</td>
</tr>
</tbody>
</table>

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 7.865 kg/kmol

| P = 4.7623E+06 Pa | V = 6.6148E-02 m**3/kg |
| P = 4.6755E+07 J/kg | H = 4.7070E+07 J/kg |
| S = 1.4662E+04 J/kg-K |

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

**OUTPUT**

Computed properties

<table>
<thead>
<tr>
<th>Independent atom</th>
<th>population</th>
<th>element potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-.9128</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
<td>-8.9536</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
<td>-52.9528</td>
</tr>
<tr>
<td>N</td>
<td>1.37000000E-04</td>
<td>41.4354</td>
</tr>
</tbody>
</table>

Products at T = 573.00 K, P = 4.700E+01 atmospheres
<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>.19301E+00</td>
<td>.10681E+00</td>
<td>.93993E-01</td>
<td>1.12724E-01</td>
</tr>
<tr>
<td>CO</td>
<td>.39445E-04</td>
<td>.21828E-04</td>
<td>.33538E-04</td>
<td>2.30369E-05</td>
</tr>
<tr>
<td>CO2</td>
<td>.21852E+00</td>
<td>.12092E+00</td>
<td>.29193E+00</td>
<td>1.27622E-01</td>
</tr>
<tr>
<td>H2</td>
<td>.43175E-02</td>
<td>.23891E-02</td>
<td>.26421E-03</td>
<td>2.52150E-03</td>
</tr>
<tr>
<td>NO</td>
<td>.23458E-03</td>
<td>.12981E-03</td>
<td>.21367E-03</td>
<td>1.37000E-04</td>
</tr>
<tr>
<td>NO2</td>
<td>.15945E-19</td>
<td>.88235E-20</td>
<td>.22628E-19</td>
<td>9.31227E-21</td>
</tr>
<tr>
<td>H2O</td>
<td>.58387E+00</td>
<td>.32310E+00</td>
<td>.31930E+00</td>
<td>3.40996E-01</td>
</tr>
</tbody>
</table>

**phase 1:** molal mass = 23.250 kg/kmol

**phase 2:** molal mass = 12.011 kg/kmol

**phase 3:** molal mass = .000 kg/kmol

* Species mols for the atom populations in mols.

**Mixture properties:** molal mass = 18.230 kg/kmol

- T = 573.00 K
- P = 4.7623E+06 Pa
- V = 3.0475E-02 m**3/kg
- U = -7.0771E+06 J/kg
- H = -6.9319E+06 J/kg
- S = 6.2309E+03 J/kg-K

Made 0 (T,P) iterations; 12 equilibrium iterations; v 3.91 IBM-PC
Appendix 3. Cellulose at Constant Specific Volume (12 ton ram, N2, N in elemental)

INPUT

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.85958700E+00</td>
</tr>
<tr>
<td>H</td>
<td>4.57188700E+00</td>
</tr>
<tr>
<td>O</td>
<td>2.39617400E+00</td>
</tr>
<tr>
<td>N</td>
<td>1.57950000E-01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.28865E+00</td>
<td>.43200E+00</td>
<td>2.85959E+00</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.46149E+00</td>
<td>.57962E-01</td>
<td>4.57189E+00</td>
</tr>
<tr>
<td>N</td>
<td>.55961E-04</td>
<td>.55517E-04</td>
<td>.96903E-04</td>
<td>5.50000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.24187E+00</td>
<td>.48221E+00</td>
<td>2.39617E+00</td>
</tr>
</tbody>
</table>

phase 1: molal mass = 7.865 kg/kmol T = 298.00 K

Calculated properties at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.28865E+00</td>
<td>.43200E+00</td>
<td>2.85959E+00</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.46149E+00</td>
<td>.57962E-01</td>
<td>4.57189E+00</td>
</tr>
<tr>
<td>N</td>
<td>.55961E-04</td>
<td>.55517E-04</td>
<td>.96903E-04</td>
<td>5.50000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.24187E+00</td>
<td>.48221E+00</td>
<td>2.39617E+00</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 28.013 kg/kmol T = 298.00 K

N2 | .10000E+01 | .79440E-02 | .27729E-01 | 7.87000E-02 |

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 8.025 kg/kmol

<table>
<thead>
<tr>
<th>P = 4.7623E+06 Pa</th>
<th>V = 6.4828E-02 m**3/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>U = 4.5456E+07 J/kg</td>
<td>H = 4.5765E+07 J/kg</td>
</tr>
<tr>
<td>S = 1.4413E+04 J/kg-K</td>
<td></td>
</tr>
</tbody>
</table>

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC
## OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent population element atom potential</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.859587E+00</td>
<td>-8.963</td>
<td>4.571887E+00</td>
<td>-8.7427</td>
</tr>
<tr>
<td></td>
<td>2.396174E+00</td>
<td>-52.1196</td>
<td>1.579500E-01</td>
<td>9.8837</td>
</tr>
</tbody>
</table>

Products at $T = 573.00$ K $P = 2.215E+02$ atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>.96756E-01</td>
<td>.68048E-02</td>
<td>.70774E-02</td>
<td>3.50744E-02</td>
</tr>
<tr>
<td>CO</td>
<td>.19575E-04</td>
<td>.13767E-05</td>
<td>.25000E-05</td>
<td>7.09595E-06</td>
</tr>
<tr>
<td>CO2</td>
<td>.24949E+00</td>
<td>.17546E-01</td>
<td>.50062E-01</td>
<td>9.04392E-02</td>
</tr>
<tr>
<td>NO</td>
<td>.59049E-26</td>
<td>.41528E-27</td>
<td>.80790E-27</td>
<td>2.14053E-27</td>
</tr>
<tr>
<td>NO2</td>
<td>.92340E-42</td>
<td>.64942E-43</td>
<td>.19370E-42</td>
<td>3.34735E-43</td>
</tr>
<tr>
<td>N2</td>
<td>.21786E+00</td>
<td>.15322E-01</td>
<td>.27826E-01</td>
<td>7.89750E-02</td>
</tr>
<tr>
<td>H2</td>
<td>.13965E-02</td>
<td>.98213E-04</td>
<td>.12836E-04</td>
<td>5.06227E-04</td>
</tr>
<tr>
<td>H2O</td>
<td>.43448E+00</td>
<td>.30557E-01</td>
<td>.35689E-01</td>
<td>1.57500E-01</td>
</tr>
</tbody>
</table>

phase 1: molal mass = 26.466 kg/kmol

phase 2: molal mass = 12.011 kg/kmol

phase 3: molal mass = 18.016 kg/kmol

Mixture properties: molal mass = 15.425 kg/kmol

$T = 573.00$ K $P = 2.2446E+07$ Pa $V = 1.5870E-03$ m**3/kg

$U = -7.4582E+06$ J/kg $H = -7.4226E+06$ J/kg $S = 4.7174E+03$ J/kg-K

WARNING! The thermochemical data for H2O(L) are extrapolated above 500 K.

Made 10 (T,P) iterations; 161 equilibrium iterations; v 3.91 IBM-PC
Appendix 4. Cellulose at Constant Specific Volume (1 ton ram, N2, N in elemental)

INPUT

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.18717000E+00</td>
</tr>
<tr>
<td>H</td>
<td>3.49684700E+00</td>
</tr>
<tr>
<td>O</td>
<td>1.83273400E+00</td>
</tr>
<tr>
<td>N</td>
<td>1.57821000E-01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 1:</td>
<td>7.865 kg/kmol T = 298.00 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.28794E+00</td>
<td>.42835E+00</td>
<td>2.18717E+00</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.46036E+00</td>
<td>.57472E-01</td>
<td>3.49685E+00</td>
</tr>
<tr>
<td>N</td>
<td>.56005E-04</td>
<td>.55425E-04</td>
<td>.96159E-04</td>
<td>4.21000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.24128E+00</td>
<td>.47814E+00</td>
<td>1.83273E+00</td>
</tr>
</tbody>
</table>

phase 2: 28.013 kg/kmol T = 298.00 K

| N2      | .10000E+01                | .10361E-01              | .35948E-01    | 7.87000E-02 |

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 8.074 kg/kmol
P = 4.7623E+06 Pa V = 6.4437E-02 m**3/kg
U = 4.5071E+07 J/kg H = 4.5378E+07 J/kg S = 1.4340E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC
OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent</th>
<th>population</th>
<th>element</th>
<th>atom</th>
<th>potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.18717000E+00</td>
<td>- .8975</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>3.49684700E+00</td>
<td>- .87047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.83273400E+00</td>
<td>- .522004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.57821000E-01</td>
<td>- 9.9659</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Products at T = 573.00 K P = 2.090E+02 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

phase 1: molal mass = 25.557 kg/kmol
| CO     | .19118E-04 | .19647E-05 | .35161E-05 | 7.69858E-06 |
| CO2    | .22475E+00 | .23096E-01 | .64944E-01 | 9.05020E-02 |
| NO     | .53185E-26 | .54656E-27 | .10479E-26 | 2.14167E-27 |
| NO2    | .76714E-42 | .78835E-43 | .23174E-42 | 3.08912E-43 |
| CH4    | .11927E+00 | .12257E-01 | .12564E-01 | 4.80290E-02 |
| H2     | .15974E-02 | .16415E-03 | .21144E-04 | 6.43232E-04 |
| H2O    | .45840E+00 | .47108E-01 | .54225E-01 | 1.84589E-01 |
| N2     | .19596E+00 | .20138E-01 | .36044E-01 | 7.89105E-02 |

phase 2: molal mass = 12.011 kg/kmol
| C       | .10000E+01 | .52282E+00 | 40121E+00 | 2.04863E+00 |

phase 3: molal mass = 18.016 kg/kmol
| H2O(L)  | .10000E+01 | .37442E+00 | .43098E+00 | 1.46713E+00 |

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 15.651 kg/kmol

T = 573.00 K P = 2.1172E+07 Pa V = 2.0570E-03 m**3/kg

U = -7.3555E+06 J/kg H = -7.3120E+06 J/kg S = 4.8149E+03 J/kg-K

WARNING! The thermochemical data for H2O(L) are extrapolated above 500 K.

Made 12 (T,P) iterations; 186 equilibrium iterations; v 3.91 IBM-PC
Appendix 5. Cellulose at Constant Specific Volume (Normal Packing, N2, N in elemental)

INPUT

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>4.20137000E-01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

phase 1: molal mass = 7.865 kg/kmol T = 298.00 K
C .29096E+00 .26795E+00 .34028E+00 7.11743E-01
H .46518E+00 .42840E+00 .45656E-01 1.13793E+00
N .56005E-04 .51577E-04 .76388E-04 1.37000E-04
O .24381E+00 .22453E+00 .37983E+00 5.96400E-01

phase 2: molal mass = 28.013 kg/kmol T = 298.00 K
N2 .10000E+01 .79060E-01 .23416E+00 2.10000E-01

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 9.458 kg/kmol
P = 4.7623E+06 Pa V = 5.5007E-02 m**3/kg
U = 3.5786E+07 J/kg H = 3.6048E+07 J/kg S = 1.2562E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT
### Computed properties

<table>
<thead>
<tr>
<th>independent</th>
<th>population</th>
<th>element</th>
<th>atom potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-8.937</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
<td>-8.6414</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
<td>-52.3116</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>4.20137000E-01</td>
<td>-9.6211</td>
<td></td>
</tr>
</tbody>
</table>

**Products at T = 573.00 K  P = 2.492E+02 atmospheres**

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>8.29461E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>9.23548E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>9.71468E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>9.75040E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>9.75040E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>3.61346E-27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO2</td>
<td>4.66365E-43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>2.10068E-01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**phase 1: molal mass = 24.947 kg/kmol**

| C(S)            | 25417E+00                  | 5.31641E-01                   |

**phase 2: molal mass = 12.011 kg/kmol**

| H2O(L)          | 1.0000E+01                 | 1.0881E+00                   | 1.51728E-01                   |

**phase 3: molal mass = 18.016 kg/kmol**

**Mixture properties:**

- **molal mass = 18.962 kg/kmol**
- **T = 573.00 K**
- **P = 2.5254E+07 Pa**
- **V = 5.0200E-03 m**
- **U = -5.5298E+06 J/kg**
- **H = -5.4030E+06 J/kg**
- **S = 5.6983E+03 J/kg-K**

**WARNING!** The thermochemical data for H2O(L) are extrapolated above 500 K.

Made 9 (T,P) iterations; 123 equilibrium iterations; v 3.91 IBM-PC
Appendix 6. Cellulose at Constant Specific Volume (10x larger reactor, N2, N in elemental)

INPUT
Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>4.78013700E+00</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 1: molal mass = 7.865 kg/kmol T = 298.00 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.14717E+00</td>
<td>.99182E-01</td>
<td>7.11743E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.23529E+00</td>
<td>.13307E-01</td>
<td>1.13793E+00</td>
</tr>
<tr>
<td>N</td>
<td>.56005E-04</td>
<td>.28328E-04</td>
<td>.22265E-04</td>
<td>1.37000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.12332E+00</td>
<td>.11071E+00</td>
<td>5.96400E-01</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 28.013 kg/kmol T = 298.00 K

| N2      | .10000E+01  | .49419E+00  | .77678E+00   | 2.39000E+00 |

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 17.822 kg/kmol

| P = 4.7623E+06 Pa  | V = 2.9192E-02 m**3/kg  | U = 1.0368E+07 J/kg | H = 1.0507E+07 J/kg | S = 7.6949E+03 J/kg-K |

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent population element atom</th>
<th>potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
</tbody>
</table>
Products at T = 573.00 K  P = 1.112E+02 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase 1: molal mass = 27.075 kg/kmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>.37898E-01</td>
<td>.32721E-01</td>
<td>.20983E-01</td>
<td>1.12733E-01</td>
</tr>
<tr>
<td>CO</td>
<td>.11424E-04</td>
<td>.98634E-05</td>
<td>.11044E-04</td>
<td>3.39826E-05</td>
</tr>
<tr>
<td>CO2</td>
<td>.43124E-01</td>
<td>.37232E-01</td>
<td>.65499E-01</td>
<td>1.28277E-01</td>
</tr>
<tr>
<td>H2</td>
<td>.12397E-02</td>
<td>.10704E-02</td>
<td>.86254E-04</td>
<td>3.68770E-03</td>
</tr>
<tr>
<td>H2O</td>
<td>.11424E+00</td>
<td>.98630E-01</td>
<td>.71028E-01</td>
<td>3.39812E-01</td>
</tr>
<tr>
<td>NO</td>
<td>.47393E-26</td>
<td>.40918E-26</td>
<td>.49081E-26</td>
<td>1.40975E-26</td>
</tr>
<tr>
<td>NO2</td>
<td>.21950E-42</td>
<td>.18951E-42</td>
<td>.34853E-42</td>
<td>6.52936E-43</td>
</tr>
<tr>
<td>N2</td>
<td>.80349E+00</td>
<td>.69372E+00</td>
<td>.77680E+00</td>
<td>2.39007E+00</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 12.011 kg/kmol

| C(S)    | .10000E+01               | .13662E+00              | .65593E-01              | 4.70699E-01 |

phase 3: molal mass = .000 kg/kmol

| H2O(L)  | .00000E+00               | .00000E+00              | .00000E+00              | .00000E+00  |

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 25.017 kg/kmol

T = 573.00 K  P = 1.1272E+07 Pa  V = 1.4610E-02 m**3/kg
U =-1.4876E+06 J/kg  H =-1.3229E+06 J/kg  S = 6.2413E+03 J/kg-K

Made 7 (T,P) iterations; 64 equilibrium iterations; v 3.91 IBM-PC
**Appendix 7. Cellulose at Constant Specific Volume (100x larger reactor, N2, N in elemental)**

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>4.83201370E+01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.26751E-01</td>
<td>.12282E-01</td>
<td>7.1174E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.42769E-01</td>
<td>.16479E-02</td>
<td>1.1379E+00</td>
</tr>
<tr>
<td>N</td>
<td>.56005E-04</td>
<td>.51492E-05</td>
<td>.27571E-05</td>
<td>1.3700E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.22416E-01</td>
<td>.13709E-01</td>
<td>5.9640E-01</td>
</tr>
</tbody>
</table>

phase 1: molal mass = 7.865 kg/kmol  T = 298.00 K

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 26.161 kg/kmol
P = 4.7623E+06 Pa  V = 1.9887E-02 m**3/kg
U = 1.2063E+06 J/kg  H = 1.3010E+06 J/kg  S = 5.9407E+03 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

**OUTPUT**

Computed properties

<table>
<thead>
<tr>
<th>Independent</th>
<th>population</th>
<th>element atom</th>
<th>element potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-.9085</td>
<td></td>
</tr>
</tbody>
</table>
### Products at $T = 573.00 \text{ K} \quad P = 9.248 \times 10^1 \text{ atmospheres}$

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$0.44419 \times 10^{-2}$</td>
<td>$0.43587 \times 10^{-2}$</td>
<td>$0.25338 \times 10^{-2}$</td>
<td>$1.09930 \times 10^{-1}$</td>
</tr>
<tr>
<td>CO</td>
<td>$0.43584 \times 10^{-5}$</td>
<td>$0.42768 \times 10^{-5}$</td>
<td>$0.43407 \times 10^{-5}$</td>
<td>$1.07865 \times 10^{-4}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$0.52269 \times 10^{-2}$</td>
<td>$0.51291 \times 10^{-2}$</td>
<td>$0.81792 \times 10^{-2}$</td>
<td>$1.29359 \times 10^{-1}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$0.46592 \times 10^{-3}$</td>
<td>$0.45719 \times 10^{-3}$</td>
<td>$0.33397 \times 10^{-4}$</td>
<td>$1.15308 \times 10^{-2}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$0.13640 \times 10^{-1}$</td>
<td>$0.13385 \times 10^{-1}$</td>
<td>$0.87376 \times 10^{-2}$</td>
<td>$3.37573 \times 10^{-1}$</td>
</tr>
<tr>
<td>NO</td>
<td>$0.18203 \times 10^{-26}$</td>
<td>$0.17862 \times 10^{-26}$</td>
<td>$0.19422 \times 10^{-26}$</td>
<td>$4.50502 \times 10^{-26}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$0.26786 \times 10^{-43}$</td>
<td>$0.26284 \times 10^{-43}$</td>
<td>$0.43817 \times 10^{-43}$</td>
<td>$6.62903 \times 10^{-43}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$0.97622 \times 10^0$</td>
<td>$0.95794 \times 10^0$</td>
<td>$0.97236 \times 10^0$</td>
<td>$2.41601 \times 10^1$</td>
</tr>
</tbody>
</table>

**Phase 2:** molal mass = $12.011 \text{ kg/kmol}$

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(S)</td>
<td>$1.00000 \times 10^1$</td>
<td>$0.18728 \times 10^{-1}$</td>
<td>$0.81508 \times 10^{-2}$</td>
<td>$4.72345 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

**Phase 3:** molal mass = $0.000 \text{ kg/kmol}$

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(L)</td>
<td>$0.00000 \times 10^0$</td>
<td>$0.00000 \times 10^0$</td>
<td>$0.00000 \times 10^0$</td>
<td>$0.00000 \times 10^0$</td>
</tr>
</tbody>
</table>

**Appendix 8. Cellulose at Constant Pressure $P = 680 \text{ psig} \approx 47 \text{ atm}$ (No N$_2$, no N in elemental)**

**INPUT**

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$7.11743 \times 10^0$</td>
</tr>
<tr>
<td>H</td>
<td>$1.13792 \times 10^0$</td>
</tr>
<tr>
<td>O</td>
<td>$5.96400 \times 10^0$</td>
</tr>
</tbody>
</table>

**Reactants at $P = 4.700 \times 10^1 \text{ atmospheres}$**
species        mol fraction    mol fraction    mass fraction      mols* in the phase     in mixture     in mixture

phase 1: molal mass = 7.865 kg/kmol  T = 298.00 K
C       .29097E+00      .29097E+00      .44436E+00      7.11743E-01
H       .46521E+00      .46521E+00      .59621E-01      1.13793E+00
O       .24382E+00      .24382E+00      .49601E+00      5.96400E-01

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties:  molal mass = 7.865 kg/kmol
P = 4.7623E+06 Pa     V = 6.6151E-02 m**3/kg
U = 4.6756E+07 J/kg   H = 4.7071E+07 J/kg   S = 1.4662E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT
Computed properties

Independent population element atom potential
      C     7.11743000E-01     -9.128
      H     1.13792900E+00     -8.9536
      O     5.96400000E-01     -52.9525

Products at T = 573.00 K  P = 4.700E+01 atmospheres

species        mol fraction    mol fraction    mass fraction      mols* in the phase     in mixture     in mixture

phase 1: molal mass = 23.250 kg/kmol
CH4       .19300E+00      .10680E+00      .93987E-01      1.12705E-01
CO        .39455E-04      .21833E-04      .33546E-04      2.30401E-05
CO2       .21863E+00      .12098E+00      .29207E+00      1.27672E-01
H2        .43174E-02      .23890E-02      .26420E-03      2.52114E-03
H2O       .58401E+00      .32316E+00      .31937E+00      3.41034E-01

phase 2: molal mass = 12.011 kg/kmol
C(S)      .10000E+01      .44665E+00      29428E+00      4.71344E-01

phase 3: molal mass = .000 kg/kmol
H2O(L)    .00000E+00      .00000E+00      .00000E+00      0.00000E+00
* Species mols for the atom populations in mols.

Mixture properties: molal mass = 18.230 kg/kmol
T = 573.00 K  P = 4.7623E+06 Pa  V = 3.0475E-02 m**3/kg
U = -7.0798E+06 J/kg  H = -6.9347E+06 J/kg  S = 6.2302E+03 J/kg-K

Made 0 (T,P) iterations; 11 equilibrium iterations; v 3.91 IBM-PC

** Appendix 9. Cellulose at Constant Volume (12 ton ram, No N2, no N in elemental) **

** INPUT **

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.85958700E+00</td>
</tr>
<tr>
<td>H</td>
<td>4.57188700E+00</td>
</tr>
<tr>
<td>O</td>
<td>2.39617400E+00</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 1: molal mass = 7.865 kg/kmol  T = 298.00 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.29097E+00</td>
<td>.29097E+00</td>
<td>.44436E+00</td>
<td>2.85959E+00</td>
</tr>
<tr>
<td>H</td>
<td>.46521E+00</td>
<td>.46521E+00</td>
<td>.59621E-01</td>
<td>4.57189E+00</td>
</tr>
<tr>
<td>O</td>
<td>.24382E+00</td>
<td>.24382E+00</td>
<td>.49601E+00</td>
<td>2.39617E+00</td>
</tr>
</tbody>
</table>

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 7.865 kg/kmol
P = 4.7623E+06 Pa  V = 6.6151E-02 m**3/kg
U = 4.6756E+07 J/kg  H = 4.7071E+07 J/kg  S = 1.4662E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

** OUTPUT **
### Computed properties

<table>
<thead>
<tr>
<th>Independent</th>
<th>population</th>
<th>element</th>
<th>atom</th>
<th>potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.859587E+00</td>
<td>-.9012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.571887E+00</td>
<td>-8.7506</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2.396174E+00</td>
<td>-52.1235</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Products at \( T = 573.00 \text{ K} \) \( P = 1.699E+02 \) atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
</tr>
<tr>
<td>phase 1: molal mass = 26.096 kg/kmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>.25298E-04</td>
<td>.13823E-05</td>
<td>.25438E-05</td>
<td>7.01944E-06</td>
</tr>
<tr>
<td>CO2</td>
<td>.32115E+00</td>
<td>.17548E-01</td>
<td>.50738E-01</td>
<td>8.91100E-02</td>
</tr>
<tr>
<td>CH4</td>
<td>.12163E+00</td>
<td>.66462E-02</td>
<td>.70050E-02</td>
<td>3.37496E-02</td>
</tr>
<tr>
<td>H2</td>
<td>.17922E-02</td>
<td>.97930E-04</td>
<td>.12971E-04</td>
<td>4.97293E-04</td>
</tr>
<tr>
<td>H2O</td>
<td>.55540E+00</td>
<td>.30348E-01</td>
<td>.35920E-01</td>
<td>1.54108E-01</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 12.011 kg/kmol

C(S) .10000E+01 .53893E+00 .42527E+00 2.73672E+00

phase 3: molal mass = 18.016 kg/kmol

H2O(L) .10000E+01 .40642E+00 .48105E+00 2.06384E+00

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 15.221 kg/kmol

\( T = 573.00 \text{ K} \) \( P = 1.7215E+07 \) Pa \( V = 1.6320E-03 \) m**3/kg

\( U = -7.6768E+06 \) J/kg \( H = -7.6487E+06 \) J/kg \( S = 4.6670E+03 \) J/kg-K

WARNING! The thermochemical data for H2O(L) are extrapolated above 500 K.

Made 12 (T,P) iterations; 288 equilibrium iterations; v 3.91 IBM-PC

---

### Appendix 10. Cellulose at Constant Volume (1 ton press, No N2, no N in elemental))

**INPUT**

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.18717000E+00</td>
</tr>
<tr>
<td>H</td>
<td>3.49684700E+00</td>
</tr>
<tr>
<td>O</td>
<td>1.83273400E+00</td>
</tr>
</tbody>
</table>
Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.29097E+00</td>
<td>.29097E+00</td>
<td>.44436E+00</td>
<td>2.18717E+00</td>
</tr>
<tr>
<td>H</td>
<td>.46521E+00</td>
<td>.46521E+00</td>
<td>.59621E+00</td>
<td>3.49685E+00</td>
</tr>
<tr>
<td>O</td>
<td>.24382E+00</td>
<td>.24382E+00</td>
<td>.49602E+00</td>
<td>1.83273E+00</td>
</tr>
</tbody>
</table>

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 7.865 kg/kmol
P = 4.7623E+06 Pa  V = 6.6151E-02 m**3/kg
U = 4.6756E+07 J/kg  H = 4.7071E+07 J/kg  S = 1.4662E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent population</th>
<th>element atom potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.18717000E+00 -.9017</td>
</tr>
<tr>
<td>H</td>
<td>3.49684700E+00 -8.7106</td>
</tr>
<tr>
<td>O</td>
<td>1.83273400E+00 -52.2054</td>
</tr>
</tbody>
</table>

Products at T = 573.00 K  P = 1.651E+02 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>.23981E-04</td>
<td>.19834E-05</td>
<td>.36106E-05</td>
<td>7.62058E-06</td>
</tr>
<tr>
<td>CO2</td>
<td>.28050E+00</td>
<td>.23199E-01</td>
<td>.66356E-01</td>
<td>8.91364E-02</td>
</tr>
<tr>
<td>H2</td>
<td>.19984E-02</td>
<td>.16528E-03</td>
<td>.21656E-04</td>
<td>6.35046E-04</td>
</tr>
<tr>
<td>CH4</td>
<td>.14686E+00</td>
<td>.12146E-01</td>
<td>.12664E-01</td>
<td>4.66674E-02</td>
</tr>
<tr>
<td>H2O</td>
<td>.57062E+00</td>
<td>.47193E-01</td>
<td>.55258E-01</td>
<td>1.81327E-01</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 12.011 kg/kmol
C(S) .10000E+01 .53389E+00 41677E+00 2.05136E+00
phase 3: molal mass = 18.016 kg/kmol
H2O(L)  .10000E+01  .38340E+00  .44893E+00  1.47313E+00

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 15.386 kg/kmol
T = 573.00 K  P = 1.6725E+07 Pa  V = 2.1344E-03 m**3/kg
U = -7.6373E+06 J/kg  H = -7.6016E+06 J/kg  S = 4.7509E+03 J/kg-K
WARNING! The thermochemical data for H2O(L) are extrapolated above 500 K.

Made 12 (T,P) iterations; 289 equilibrium iterations; v 3.91 IBM-PC

** Appendix 11. Cellulose at Constant Volume (10 x larger reactor, No N2, no N in elemental)

**INPUT**

Computed properties

atoms population
C 7.11743000E-01
H 1.13792900E+00
O 5.96400000E-01

Reactants at P = 4.700E+01 atmospheres

species mol fraction mol fraction mass fraction mols*
in the phase in mixture in mixture

phase 1: molal mass = 7.865 kg/kmol  T = 298.00 K
C .29097E+00 .29097E+00 .44436E+00 7.11743E-01
H .46521E+00 .46521E+00 .59621E-01 1.13793E+00
O .24382E+00 .24382E+00 .49601E+00 5.96400E-01

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 7.865 kg/kmol
P = 4.7623E+06 Pa  V = 6.6151E-02 m**3/kg
U = 4.6756E+07 J/kg  H = 4.7071E+07 J/kg  S = 1.4662E+04 J/kg-K
OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent population</th>
<th>element atom</th>
<th>potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-.9152</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
<td>-.91463</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
<td>-53.3355</td>
</tr>
</tbody>
</table>

Products at T = 573.00 K P = 2.182E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols* in the phase</th>
<th>in mixture</th>
<th>in mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase 1: molal mass = 23.215 kg/kmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>.57814E-04</td>
<td>.31989E-04</td>
<td>.49205E-04</td>
<td>3.37948E-05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>.21843E+00</td>
<td>.12086E+00</td>
<td>.29210E+00</td>
<td>1.27684E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>.19183E+00</td>
<td>.10614E+00</td>
<td>.93511E-01</td>
<td>1.12135E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>.63249E-02</td>
<td>.34997E-02</td>
<td>.38744E-03</td>
<td>3.69722E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>.58335E+00</td>
<td>.32278E+00</td>
<td>.31934E+00</td>
<td>3.40998E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 2: molal mass = 12.011 kg/kmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(S)</td>
<td>.10000E+01</td>
<td>.44668E+00</td>
<td>29462E+00</td>
<td>4.71891E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 3: molal mass = .000 kg/kmol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O(L)</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
<td>0.00000E+00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 18.210 kg/kmol

<table>
<thead>
<tr>
<th>T = 573.00 K</th>
<th>P = 2.2107E+06 Pa</th>
<th>V = 6.5589E-02 m**3/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>U = -7.0774E+06 J/kg</td>
<td>H = -6.9324E+06 J/kg</td>
<td>S = 6.4285E+03 J/kg-K</td>
</tr>
</tbody>
</table>

Made 14 (T,P) iterations; 207 equilibrium iterations; v 3.91 IBM-PC
Appendix 12. Cellulose at Constant Volume (100 x larger reactor, No N2, no N in elemental)

INPUT

Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
</tr>
<tr>
<td>phase 1: molal mass = 7.865 kg/kmol</td>
<td>T = 298.00 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.29097E+00</td>
<td>.29097E+00</td>
<td>.44436E+00</td>
<td>7.11743E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46521E+00</td>
<td>.46521E+00</td>
<td>.59621E+00</td>
<td>1.13793E+00</td>
</tr>
<tr>
<td>O</td>
<td>.24382E+00</td>
<td>.24382E+00</td>
<td>.49601E+00</td>
<td>5.96400E-01</td>
</tr>
</tbody>
</table>

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 7.865 kg/kmol
<table>
<thead>
<tr>
<th>P</th>
<th>4.7623E+06 Pa</th>
<th>V = 6.6151E-02 m**3/kg</th>
<th>U = 4.6756E+07 J/kg</th>
<th>H = 4.7071E+07 J/kg</th>
<th>S = 1.4662E+04 J/kg-K</th>
</tr>
</thead>
</table>

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT

Computed properties

<table>
<thead>
<tr>
<th>Independent population element</th>
<th>atom</th>
<th>element potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-.9171</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
<td>-9.7283</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
<td>-54.4824</td>
</tr>
</tbody>
</table>

Products at T = 573.00 K P = 2.193E+00 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction</th>
<th>mol fraction</th>
<th>mass fraction</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in the phase</td>
<td>in mixture</td>
<td>in mixture</td>
<td></td>
</tr>
</tbody>
</table>
phase 1: molal mass = 23.025 kg/kmol

CO       .18233E-03  .10103E-03  .15623E-03  1.07303E-04
CO2      .21880E+00  .12125E+00  .29458E+00  1.28770E-01
CH4      .18576E+00  .10294E+00  .91167E-01  1.09324E-01
H2       .19649E-01  .10888E-01  .12118E-02  1.15636E-02
H2O      .57560E+00  .31896E+00  .31724E+00  3.38754E-01

phase 2: molal mass = 12.011 kg/kmol

C(S)      .10000E+01  .44587E+00  .29565E+00  4.73542E-01

phase 3: molal mass = 0.000 kg/kmol

H2O(L)    .00000E+00  .00000E+00  .00000E+00  0.00000E+00

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 18.114 kg/kmol

T = 573.00 K    P = 2.2224E+05 Pa
V = 6.5589E-01 m**3/kg

U = -7.0604E+06 J/kg
H = -6.9146E+06 J/kg
S = 7.0419E+03 J/kg-K

Made 22 (T,P) iterations; 295 equilibrium iterations; v 3.91   IBM-PC

Appendix 13. Cellulose at Constant Pressure P =680 psig ~47 atm (with N2 and N in elemental)

We also tried introducing the nitrogen gas as an initial reactant. The moles of nitrogen (0.21 moles) introduced were calculated on the excel file of March 13, 2015.

Table appendix 13, 1: Stanjan input conditions for Avicel Cellulose at a constant pressure including nitrogen gas as one of the input reactants

<table>
<thead>
<tr>
<th>Feed</th>
<th>Type of process</th>
<th>Moles of initial reactants</th>
<th>Initial T (K)</th>
<th>Initial P (atm)</th>
<th>Final Gas products</th>
<th>Final T (K)</th>
<th>Final P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel Cellulose</td>
<td>Constant P</td>
<td>C 0.711743</td>
<td>H 1.137929</td>
<td>298</td>
<td>47</td>
<td>CO, CO2, NO, NO2, N2, CH4, H2, H2O</td>
<td>C(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0.5964</td>
<td>N 0.000137</td>
<td>N2 0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fixed carbon yield amounts up to 29.429% (see Appendix 3). The fixed carbon yield when we have nitrogen as one of the initial gases should be calculated as

\[
\text{Fixed Carbon Yield (\%)} = \frac{\text{mass fraction } C(s)}{(1 - \text{mass fraction } N_2)} \cdot 100 = \frac{0.22538}{1 - 0.23416} \cdot 100 = 29.429\% 
\]

We can conclude that the introduction of the nitrogen as an input species does not have an effect on the final result of the fixed carbon yield.
INPUT
Computed properties

<table>
<thead>
<tr>
<th>atoms</th>
<th>population</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
</tr>
<tr>
<td>N</td>
<td>4.20137000E-01</td>
</tr>
</tbody>
</table>

Reactants at P = 4.700E+01 atmospheres

<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>.29096E+00</td>
<td>.26795E+00</td>
<td>.34028E+00</td>
<td>7.11743E-01</td>
</tr>
<tr>
<td>H</td>
<td>.46518E+00</td>
<td>.42840E+00</td>
<td>.45656E+00</td>
<td>1.13793E+00</td>
</tr>
<tr>
<td>N</td>
<td>.56005E-04</td>
<td>.51577E-04</td>
<td>.76388E-04</td>
<td>1.37000E-04</td>
</tr>
<tr>
<td>O</td>
<td>.24381E+00</td>
<td>.22453E+00</td>
<td>.37983E+00</td>
<td>5.96400E-01</td>
</tr>
</tbody>
</table>

phase 2: molal mass = 28.013 kg/kmol  T = 298.00 K
N2     .10000E+01    .79060E-01    .23416E+00    2.10000E-01

Calculations made using frozen composition.

* Species mols for the atom populations in mols.

Mixture properties: molal mass = 9.458 kg/kmol
P = 4.7623E+06 Pa  V = 5.5007E-02 m**3/kg
U = 3.5786E+07 J/kg  H = 3.6048E+07 J/kg  S = 1.2562E+04 J/kg-K

Made 0 (T,P) iterations; 0 equilibrium iterations; v 3.91 IBM-PC

OUTPUT
Computed properties

<table>
<thead>
<tr>
<th>atom</th>
<th>population</th>
<th>element potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.11743000E-01</td>
<td>-9.128</td>
</tr>
<tr>
<td>H</td>
<td>1.13792900E+00</td>
<td>-9.0308</td>
</tr>
<tr>
<td>O</td>
<td>5.96400000E-01</td>
<td>-53.1060</td>
</tr>
<tr>
<td>N</td>
<td>4.20137000E-01</td>
<td>-10.5620</td>
</tr>
</tbody>
</table>

Products at T = 573.00 K  P = 4.700E+01 atmospheres
<table>
<thead>
<tr>
<th>species</th>
<th>mol fraction in the phase</th>
<th>mol fraction in mixture</th>
<th>mass fraction in mixture</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>.14172E+00</td>
<td>.88936E-01</td>
<td>.71880E-01</td>
<td>1.12562E-01</td>
</tr>
<tr>
<td>CO</td>
<td>.33840E-04</td>
<td>.21235E-04</td>
<td>.29966E-04</td>
<td>2.68767E-05</td>
</tr>
<tr>
<td>CO2</td>
<td>.16083E+00</td>
<td>.10092E+00</td>
<td>.22377E+00</td>
<td>1.27735E-01</td>
</tr>
<tr>
<td>H2</td>
<td>.36996E-02</td>
<td>.23216E-02</td>
<td>.23579E-03</td>
<td>2.93837E-03</td>
</tr>
<tr>
<td>H2O</td>
<td>.42922E+00</td>
<td>.26935E+00</td>
<td>.24447E+00</td>
<td>3.40902E-01</td>
</tr>
<tr>
<td>NO2</td>
<td>.30714E-42</td>
<td>.19274E-42</td>
<td>.44674E-42</td>
<td>2.43943E-43</td>
</tr>
<tr>
<td>N2</td>
<td>.26449E+00</td>
<td>.16598E+00</td>
<td>.23424E+00</td>
<td>2.10068E-01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase 2:</td>
<td>molal mass = 12.011 kg/kmol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(S)</td>
<td>.10000E+01</td>
<td>.37247E+00</td>
<td><strong>22538E+00</strong></td>
<td>4.71419E-01</td>
</tr>
<tr>
<td>phase 3:</td>
<td>molal mass = .000 kg/kmol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O(L)</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
<td>0.00000E+00</td>
</tr>
</tbody>
</table>

* Species mols for the atom populations in mols.

Mixture properties:  
- molal mass = 19.850 kg/kmol  
- T = 573.00 K  
- P = 4.7623E+06 Pa  
- V = 3.1710E-02 m**3/kg  
- U =-5.3930E+06 J/kg  
- H =-5.2420E+06 J/kg  
- S = 6.4180E+03 J/kg-K  

Made 0 (T,P) iterations; 11 equilibrium iterations; v 3.91 IBM-PC