Charcoal 'mines' in the Norwegian woods

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ABSTRACT:

This paper 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 CO_2 emissions by increasing the use of charcoal as a substitute for coal and coke in the reduction process. As charcoal is not produced in Norway, large amounts of it are imported from South-Asia. Norway now intends to produce charcoal locally using optimum carbonization techniques from local biomass and forestry waste. That is where the pressurized flash carbonization experiments come in. Birch, spruce and forest residue or GROT samples (GRener Og Topper, i.e. branches and tops) were carbonized, enabling the analysis of the impact of pressure and FC canister insulation on their respective fixed carbon yields. Forest residue (FR) proved to be proper to make charcoal, as fixed carbon contents of 80% could be achieved at moderate pressures. The fixed carbon yields of spruce and birch wood reached over 90% of their theoretical values. The high charcoal yields can result in remarkable cost savings for the metallurgical industry, while at the same time making excessive deforestation unnecessary. The use of coal will soon be abandoned and charcoal 'mines' could become an obvious choice.

1.Introduction

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[1], 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 countries like Brazil and Norway to mention just a few.

Arguments against charcoal are that it is very fragile, ignites easily at low temperatures, and

can show hygroscopic characteristics in humid environments[2].

Charcoal was the preferred reducing agent for blacksmiths in the Middle Ages[3], but was

gradually replaced by coal despite charcoal's superior characteristics. In 1901, it was still

common to use charcoal rather than coal to make ferrosilicons with a purity of 75% and

higher[4]. Later in the 20th century the switch to coal was obvious 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[5]), causing massive deforestation and CO_2 emissions[6]. The combination of enormous lignocellulosic resources (the Amazonian rain forest in Brazil covers more than 5,500,000 km^2), and the lack of deforestation rules have resulted in over 50% of Brazilian charcoal originating from native forests[7].

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 currently investigating the cost issues. Charcoal is not cheap: various papers report prices between 162 and 780 $/tonne[8, 9]. The coal price in the US in 2013 lied between 10-60 $/tonne, depending on the grade of coal[10].

On the whole, 77% of the world's silicon (which totals 7,680,000 metric tonnes/year) 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[11]. The silicon production industry of Norway had a world's share of 9% in 2012. Norway is also one of world's main exporters of ferrosilicon and ferromanganese[12]) with a share of 4%[13].

A quick calculation provides an excellent illustration of the issues that are at stake. The equation for carbothermic reduction of silica into silicon is: $SiO_2 + 2C => Si + 2CO$ where 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.

For an annual production of 369,000 metric tonnes of silicon, 453,870 metric tonnes of charcoal are needed.

Assuming a carbonization with a modest yield of 25% is used, a total of 1,815,480 metric tonnes of dry wood are needed. Transportation of charcoal from countries like South Asia should be avoided as it would double the charcoal cost[14]. Norway however can resort to alternative options. This is what led us to investigate the manufacture of charcoal using 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 a great many 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[15], so an average of 600 kg of freshly cut wood/m^3 will be used in this analysis.

Only two-thirds of a tree will be hauled to a processing factory[16]; 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 1320000 metric tonnes. Using the whole tree (and all forest residues) brings us closer to the amount of tonnage needed to supply admittedly only the ferrosilicon industry in Norway.

Flash carbonization (FC) may be a fast and economical way to use Norwegian birch or spruce -or even their forest residues - to make the fixed-carbon containing charcoal necessary for the ferrosilicon industry. In support of the Norwegian ferrosilicon industry, local birch, spruce and forest residues were carbonized in the FC reactor, with a view to analyzing the impact of

pressure and feedstock (soft- versus hardwood) on their respective charcoal and fixed carbon yields. The produced high quality charcoals were analyzed using different state of the art techniques.

2. Apparatus and experimental procedures

Many papers on biomass carbonization using the FC apparatus were published using any feedstock imaginable, including leucaena[17] and oak wood, corncobs (the most abundant agricultural waste product in the US)[18, 19], macadamia nutshells from the Big Island of Hawaii, wood sawdust, Christmas tree chips, Hungarian sunflower shells[20], coconut, eucalyptus, bana grass[21], alder, birch, pine and spruce wood, rice hulls, sewage sludge[22, 23] and garlic processing waste[24].

It was not until 2015 that the FC apparatus in the R^3-laboratory in Hawaii was partly rebuilt and modernized. 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 a high temperature carbon steel seamless pressure pipe (6" diameter, 39" long) to which two blind carbon steel weld neck flanges are attached. It might be interesting to note that the steel pipe was manufactured in Brazil, the 9th largest crude steel producer (at 34.2 million tonnes in 2013)[25], and that (unsustainable and probably low yield) charcoal was used to fire the furnaces to create the steel.

The bottom flange 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 R^3-Laboratory. The heating element is housed in a steel round casing, which works as a support for the FC canister. The upper flange accommodates an air inlet, TC inlets and 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 made to function as a quick-opening closure.

All lines are made of Swagelok tubes and connections. In general, all Swagelok air inlet lines are 0.6 cm in diameter, while the lines that carry the exhaust (together with the safety lines) are either 0.95 cm or 2.54 cm. All these Swagelok lines are rated at 21.5 MPa at 37°C, (down)rated 18.3MPa at 300°C using ASTM A269.

Figure 1 shows the most updated setup of the FC reactor as of 2016. 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 0.6 cm Swagelok lines, while normal lines are 0.95 cm. Close to the stack in the right upper corner of Figure 1, the lines are 2.54 cm wide in diameter.

Figure 1: Schematic of the FC apparatus with AC: 4 cylinder air-cart, ACT: atmospheric condensates trap, DDV: downdraft valve, IV: isolation valve, MMV: micrometer valve, PCT: pressurized condensates trap, PAV: pneumatically activated valve, SLRV: spring-loaded

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) 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 and operating pressure, 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.

The ultimate safety mechanism is the carbon steel rupture disc holder that houses a burst diaphragm that is rated at 2.77 MPa. This burst diaphragm is directly connected to the top of the reactor vessel. Another pressure release mechanism is the spring-loaded relief valve, in which the valve seat is forced against the valve inlet nozzle by a factory-installed and calibrated spring. A CO alarm is attached beneath the exhaust, to warn operators if CO levels become too high.

Loading the FC vessel with biomass is fairly easy, but when charcoal is made, it could 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 for the FC apparatus 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 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 is a mesh which supports the loaded biomass and depending on the particle size of the biomass, a finer or coarser mesh is used. The adjustment of the mesh to the particle size prevents particles, tars and ash getting into the exhaust lines, where they would cause clogs after cooling down.

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 to the cylinder via an Aramide/Nitrile gasket, which has to be replaced regularly, depending on the severity and duration of the experiment. A steel cable connected to the FC canister, makes 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 1 the air supply is shaded in blue. 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 SS316 line via a Swagelok quick-connect.

The direct connection to the air supply lines 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 Swagelok line is long enough to stick out of the top flange, for easy insertion of several (0.1016 cm diameter) type K sub-mini thermocouples into the FC canister and TC holder. Installing several thermocouples and creating an interface in a pressure vessel (without thermowells) containing hot gases is complicated, but it was accomplished using a Conax-brand compression seal fitting. With the current configuration, up to eight thermocouples can be placed in the middle of any biomass bed at different heights. Because no thermowell was used, instantaneous temperature readings were possible. 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 steel reactor vessel. The IDs were measured with a dial caliper (which reads accurately to .001") as 10.9 cm and 7.0 cm, respectively.

2.1 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). Air was used during FC experiments to pressurize the reactor

and to allow combustion of part of the feed (which releases heat), 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 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 pressurized (PCT) conditions; see Figure 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.

During an experiment, the temperatures and pressures (see Figure 1 for locations) are

measured with Type K thermocouples, monitored and recorded with NI equipment using NI

LabVIEW using 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) 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.

The spruce or birch wood and their forest residues are subjected to a moisture content

analysis according to ASTM E 1756 Method A at 105°C in a convection oven prior to every

experiment. The charcoal moisture content is analyzed using a vacuum oven. Subsequently,

the charcoal is ground using a mill below 20 mesh and loaded into 35x29mm porcelain

crucibles that are subjected to 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° for the volatile matter

and ash content analysis, respectively. All values are given on an oven dry basis, except for

the moisture content values, which are on a wet basis.

Ultimate (according to ASTM D 3176 and D5373, ash analysis done at 750°C for 8 h)

analyses (see Table 1) were done by the SINTEF Energy Research.

The microstructures, surface topographies and sizes of charcoal particles were analyzed

using a Hitachi S-3400N emission scanning microscope (SEM). The SEM works in

conjunction with an energy dispersive X-ray (EDX) spectroscope (Bruker Quantax). The

elemental compositions of selected spots were analyzed by the EDX. Prior to the scans, the

samples were mounted on carbon tape (without coating). The concentrations of inorganic

elements were measured using inductively coupled plasma optical emission spectroscopy

(ICP-OES) according to standard CEN/TS 15290:2006 and are displayed in Table 5.

2.2 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[26] (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).

Norwegian spruce makes up 45% of the forest in Norway, being the dominant type of wood[27].

The birch tree is native to Northern Europe and the most common hardwood in Norway at

16% of the forest[27]. The extractive-rich bark of the birch tree is used in Sweden to make

bread[28] and refreshing drinks[29]. Iceland turns it into a sweet liqueur named Birkir or Bjork, believed to benefit skin and hair.

Forest residues or GROT (an acronym for GRener Og Topper, 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[30]. 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[31].

The Norwegian spruce and birch was delivered in February and 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 1. 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 Norwegian birch wood contains considerable amounts of bark of substantial size. These large amounts of birch bark do not come as a surprise, as birch bark easily comes off its wood after drying, whereas the spruce bark adheres more tightly to the wood branches and chips. The Norwegian spruce wood contains bark but in smaller amounts (and in smaller pieces) compared to birch. The spruce bark is harder (and does not have a leather feel) 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 birch forest residue wood contains 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.

A large portion of the spruce forest residue 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. These wood chips are expected to have the lowest ash content and during pyrolysis will behave much like true spruce stem wood.

Previous FC work has shown that carbonization of larger wood particles gives rise to higher fixed carbon yields[32]. 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), and only the larger fraction was used. The spruce and birch forest residue was used unchanged. This way the carbonization of the forest residue would approximate a real life scenario, heterogeneity being the main difficulty in creating high quality charcoal from forest residue.

Table 1 shows the higher ash contents of forest residue 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 forest residue sample was ground below 40 mesh to ensure that a representative sample was being used. The ash content of different parts of Norwegian spruce

varied 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[33]. The

theoretical fixed carbon yields in Table 1 were calculated using a thermochemical equilibrium

solver to determine the preferred products of biomass pyrolysis. The values obtained from

these simulations allowed for the establishment of a benchmark for comparing experimental

fC yields. One of those solvers (and the preferred solver in the R[3]-Laboratory) is

STANJAN[34], which was used to calculate the mass fraction of solid carbon (which can be

converted into an fC yield) at thermochemical equilibrium. STANJAN solves adiabatic

equilibrium calculations numerically in single or multiphase systems.

When the FC canister was loaded, the canister was tapped with a rubber hammer to remove

any large air pockets from the wood bed.

Table 1 shows ultimate analyses of the different wood samples. It shows that spruce and birch

have very similar carbon contents while those of their respective forest residues are slightly

higher. Both the spruce and birch forest residue have elevated nitrogen (and in lesser amounts

also sulfur) contents compared to the pure wood samples.

Table 1: Ultimate analyses of spruce and birch woods together with their respective forest residues and the calculated theoretical fixed-carbon yields yfC

feed	MC[b] (wt %,wb)	Proximate Analysis [a] (wt%, db)			ultimate analysis[c] (wt %,db)						y_{fC}[d] (wt %,daf)
		VM	fC	Ash	C	H	O	N	S	Ash	
spruce	9.8	73.1	26.5	0.37	49.64	6.40	43.25	0.13	0.02	0.56	33.8
spruce FR	8.9	70.0	28.5	1.5	51.66	6.13	38.89	0.68	0.14	2.5	37.7
birch	8.4	80.2	19.5	0.34	49.93	6.72	42.11	0.26	0.02	0.95	33.9
birch FR	8.0	74.9	23.5	1.6	50.74	6.32	40.89	0.84	0.04	1.17	35.6

[a]Proximate analysis done according to ASTM standards E871, E872 and D1102 [b]Using ASTM D1102 in the R^3-Laboratory, wet mass basis. [c]Dry mass basis, SINTEF Energy Research. [d]Using STANJAN at constant pressure, dry ash-free feed.

3. Results and Discussion

In the previous section it has been 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[35]. Much like in Iceland, Uzbekistan now has to import large

amounts of birch charcoal to keep manufacturing over 18,000 tonnes of silicon a year[36].

Bioenergy production from forest 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, reduce forest productivity[37]. Forest residues typically contain more ash and extractives because of the presence of the needles and bark[38]. These residues are richer in nitrogen compounds and are very heterogeneous in texture and chemical composition.

The chemical differences between softwood spruce, hardwood birch and their forest residues 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%)[39]. Birch wood contains 22% lignin, which is less compared to spruce, and 23% hemicellulose, which is more compared to spruce[40]. In addition to higher lignin contents[41], conifers such as spruce also possess large amounts of extractives, resulting in a higher energy content[42]. That is why lignin and extractive-rich bark and branches of softwoods have a higher calorific value than stem wood[43]. These extractives are a complex mixture of low molecular weight sugars, inositols, amino acids, simple fats, carboxylic acids, terpenes, and phenolic compounds[38]. Extractive-free wood possibly favors char and gas yields during pyrolysis[41]. Furthermore, hardwoods typically have higher densities compared to softwoods, and external factors like silviculture practices can alter density[44]. The main biomass constituent that favors char formation was found to be lignin[41]. 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[45].

Birch[46] and spruce[47] 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 Fagernäs et al[46], while in another publication[48], 79.6% fixed carbon birch charcoal was made with a charcoal yield of 34%. If we use an ash content of 0.6%, a resulting 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 (not charcoal!) yields[49].

Wang et al[50] evaluated the effect of sample size and pressure on the fixed carbon yields of spruce wood and forest residue by using atmospheric and pressurized TGAs. The fixed carbon yield increased from 18.89 to 24.58% when the pressure was raised to 2.2 MPa. Surprisingly, the forest residue has higher fC contents compared to the wood, but as expected, larger ash contents.

The conditions of ten FC runs are displayed in Table 2. Each FC experiment loaded 2 kg +/- 3% of either birch wood, spruce wood or their forest residues. Their moisture contents (on a wet basis) averaged out to 10% +/- 0.5%. The last 2 experiments (9 & 10) were done with a more insulated, but smaller canister (3.5" OD, an area decrease of 2.4 times compared to the larger canister) to evaluate possible positive enhancements due to a smaller, and better insulated canister.

Table 2: List of FC experiments conducted at different reactor pressures using different types of Norwegian wood.

Experiment Number [#]	Experiment Date [yymmdd]	Feed Stock	Reactor Pressure [MPa]	Remarks[a]
1	150702	birch	0.79	
2	150508	birch	2.17	FP
3	150219	spruce	0.79	
4	150212	spruce	2.17	FP
5	150716	birch FR	0.79	pOt
6	150513	birch FR	2.17	FP, pOt
7	150713	spruce FR	0.79	pOt
8	150512	spruce FR	2.17	FP, pOt
9	150506	spruce	0.79	
10	150720	spruce	2.17	FP

[a]FP=Fused particles, pOt=partly overcarbonized top.

During the higher pressure experiments at 2.14 MPa, deflagrations occurred during the initial six minutes of heating. During experiment number 4 (see Table 2) the pressure rose slowly from 2.17 MPa to 2.27 MPa whereupon it spiked to 2.47 MPa in less than 5 seconds until the downdraft valve was opened to allow the gases to escape. Experiment number 8 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 600°C 15 cm above the heater at the time of the deflagrations) but equally well by the devolatilized gases from the biomass bed. Sam Wade[51] investigated deflagrations of corncob (which are the most vigorous) in the FC lab-scale unit and observed a maximum pressure spike between 0.42 and 1.31 MPa with dP/dt rates of 0.34-1.21 MPa/s.

Figure 2 exhibits typical time-temperature behavior of 5 type K thermocouples located at various heights from the heater in the birch wood feed bed, during experiment 2 (carbonization at a reactor pressure of 2.17 MPa). After twenty minutes into the experiment, temperatures in excess of 700°C were observed while the heater was turned off after 6 minutes.
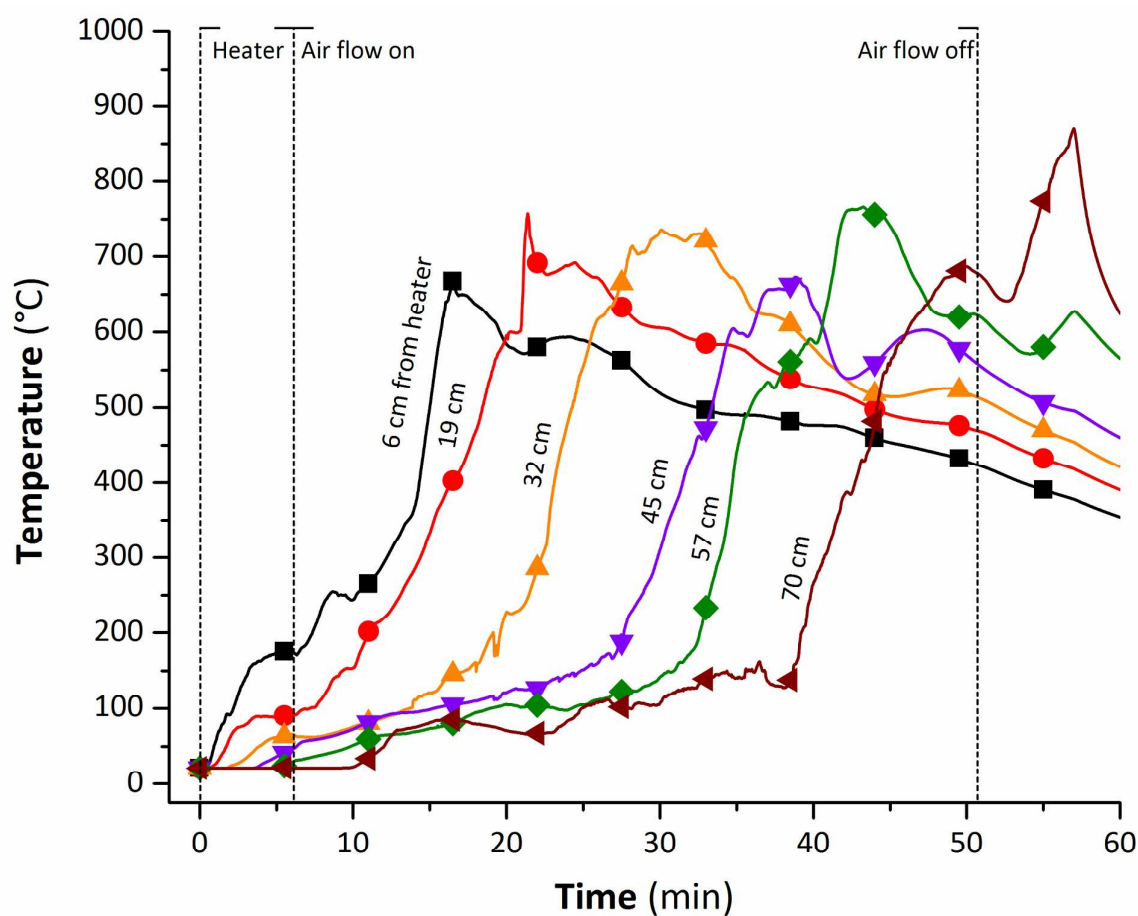

Figure 2: Measured centerline temperature profile at different heights during FC experiment 2.

Figure 3 shows spruce wood, the carbonized spruce wood and carbonized wood fragments

from experiment number 4 in Table 2 completed at a higher reactor pressure of 2.17 MPa. At

these higher pressures, charcoal particles tend to be glued to each other with a charcoal-like

material that had the appearance of solidified tar. Experiments 2 and 4 and 6, 8 and 10 with

reactor pressures of 2.17 MPa all showed these fused charcoal particles. The fused particles of

experiment number 2 were subjected to a proximate analysis and the results showed that the

fused tar-like substance had fC contents of 92% while the surrounding charcoal particles had

fC contents of 78%.

Figure 3: Spruce wood feed, spruce wood charcoal on the bottom and a fused particle originating from experiment 4 in Table 2.

In Table 3 the results of the experiments of Table 2 are shown and one of the most important

factors of the experiments are the charcoal yield (ychar) and the fixed-carbon yield (yfC)

which are defined as follows:

$$y_{char} = \frac{M_{char}}{M_{feed}}$$

where M_{char} and M_{feed} represent the dry masses of charcoal and feedstock, respectively. The

fixed-carbon yield incorporates the composition of the charcoal (determined by the proximate

analysis) into the charcoal yield:

$$y_{fC} = y_{char}(\frac{\%fC}{100-\%feed\ ash})$$

where %fC and %feed ash denote the percentage of fixed-carbon contained in the charcoal

and the percentage of ash in the feedstock, respectively.

Table 3: Results of the FC experiments displayed in Table 2 conducted at different reactor pressures.

Experiment Number	Feed Stock	Reaction Time[a]	Reactor Pressure	Size Canister	Proximate analysis[b]			Charcoal yield	fC yield[d]
[#]		Min	MPa		wt%, db[c]			wt%, db	wt%, daf
					VM	fC	Ash		
1	birch	51	0.79	Large	6.6	91.4	2.0	23.9	21.9
2	birch	39	2.17	Large	20.3	78.3	1.4	40.0	31.4
3	spruce	28	0.79	Large	18.1	80.2	1.7	33.5	26.9
4	spruce	22	2.17	Large	18.8	80.1	1.1	38.2	30.7
5	birch FR	52	0.79	Large	13.1	80.7	6.1	32.2	26.4
6	birch FR	47	2.17	Large	28.5	67.7	3.7	37.0	25.5
7	spruce FR	60	0.79	Large	12.0	83.8	4.2	30.5	26.0
8	spruce FR	52	2.17	Large	22.3	72.7	5.0	36.9	27.3

				Small					
9	spruce	59	0.79		13.0	85.8	1.2	24.1	20.7
10	spruce	52	2.17	Small	22.3	72.7	5.0	36.9	27.3

[a]Time from heater on to air off. [b]Proximate analysis done according to ASTM D1762 – 84. [c]db= reported on a dry basis. [d]fC yield= Charcoal yield*(fC%/(100-feed ash%)) hence reported on a daf= dry ash-free basis.

As explained earlier, a second smaller 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.

As experiment 9 in Table 3 shows, 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%, experiment 9 and 3, respectively).

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 experiment 1, 6.1 kg of steel canister was present per kg of feed while during experiment 9, 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.

The ash content is not influenced by the canister used (and the change in heat migration), but seems rather dependent on the charcoal yield which is dependent on the pressure in the system (which in turn influences heat transfer).

The benefits of operating the FC reactor at higher pressures have been demonstrated in earlier publications[8, 17, 20, 21, 23, 32, 51-53]. Table 3 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, a characteristic 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 produced at 2.17 MPa also has a higher fixed carbon yield (31.2% versus 27.0%).

The birch wood (experiment 2 in Table 2) was carbonized for an extended period of time, and as a result the full bed was completely carbonized (and significantly devolatilized).

Due to the very low charcoal yield, the fixed carbon yield was equally low in experiment 2. 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.

Despite the longer reaction time needed for carbonizing spruce and birch forest residue compared to the spruce and birch, the forest residues have reduced fixed carbon contents by almost 10%. The ash content of the forest residue charcoals is a lot larger than the ash content of the spruce or birch wood charcoal, but this is merely because the forest residue feed contains large amounts of ash to begin with. The fixed carbon contents of the birch forest

residue is a lot lower compared to the fixed carbon content of the birch wood, despite the longer reaction time of the forest residue sample. When either spruce or birch wood is compared to their respective forest residues, 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 forest residue charcoal, the fixed carbon yield is low as well. The forest residue was loaded as received. It 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[54] when larger particles were carbonized.

On the other hand, the forest residue ash content might have boosted its fixed carbon yields as evidenced by previous work in the R^3-Laboratory[8]. It should be pointed out that the forest residue is neither fine nor coarse. It is a mixture that is similar to genuine forest residue waste that does not need any processing. Bearing that in mind, the results for the forest residue are promising.

It is important to have a measurement of uncertainty factors. As 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 was 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 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/tonne or $0.100/kg) and the kg of dry wood harvested per year as in:

$$\frac{\text{kg dry wood}}{\text{year}} = \frac{100{,}000{,}000\,\frac{kg\,fC}{year}}{Yield\,(\frac{kg\,char}{kg\,dry\,wood})\,*\,\text{fC content}\,(\frac{kg\,fC}{kg\,char})}$$

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 (kg char / kg dry wood) and the fC content (kg fC / kg char) of the charcoal as shown as follows: (mass fC+VM+Ash) / (mass feed).

Table 4 compares the benefits of operating at higher pressures by using the fC content and charcoal yields from FC experiment 3 and 4 (which operated at 2.17 and 0.79 MPa, respectively), and inputs these in the equation below. Table 4 shows that by operating at 2.17 MPa, The company Elkem in Norway can save over 5 million $ every year. Furthermore, the

$$\frac{\frac{\$}{\text{year}}}{} = \frac{\frac{kg\,dry\,wood}{year}}{} * 0.100\,\frac{\$}{kg\,dry\,wood}$$

company 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 4: Benefits of producing charcoal at higher pressures.

Reactor Pressure	0.79 Mpa	2.17 Mpa
Charcoal Yield (wt%, db)	33.5	39.0
fC content Char (wt%, db)	80.1	79.6
kg dry wood/year	373,000,000	322,000,000
kg wet wood/year	1,120,000,000	966,000,000
$/year	**$37,300,000**	**$32,200,000**

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[17] 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[10], respectively.

The proximate analysis which was originally developed to classify a spectrum of coal varieties, offers key insights into the origin, production, and utility of the charcoal. The proximate analysis determines the volatile matter content, ash content and fixed-carbon content on a dry basis. These three variables as displayed on a ternary plot in Figure 4 sum up to 100%. The dashed line indicates that a volatile matter content has to be lower than 30%, in order to call a char, real charcoal. If the ash content is smaller than 5%, we have domestic use charcoal (for developing countries). Heavily devolatilized charcoal with volatile matter contents below 15% and ash contents of maximum 5% are high quality metallurgical charcoals. Charcoal produced at 0.79 MPa is of a higher quality compared to charcoal at 2.17 MPa. Birch wood and forest residue charcoal shows a larger range of qualities, because of the heterogeneity of the feed.

All charcoals made have less than 10% of ash, which is perfect, as higher than 12% ash

contents creates more slag. Even the forest residue charcoal (which initially had a higher ash

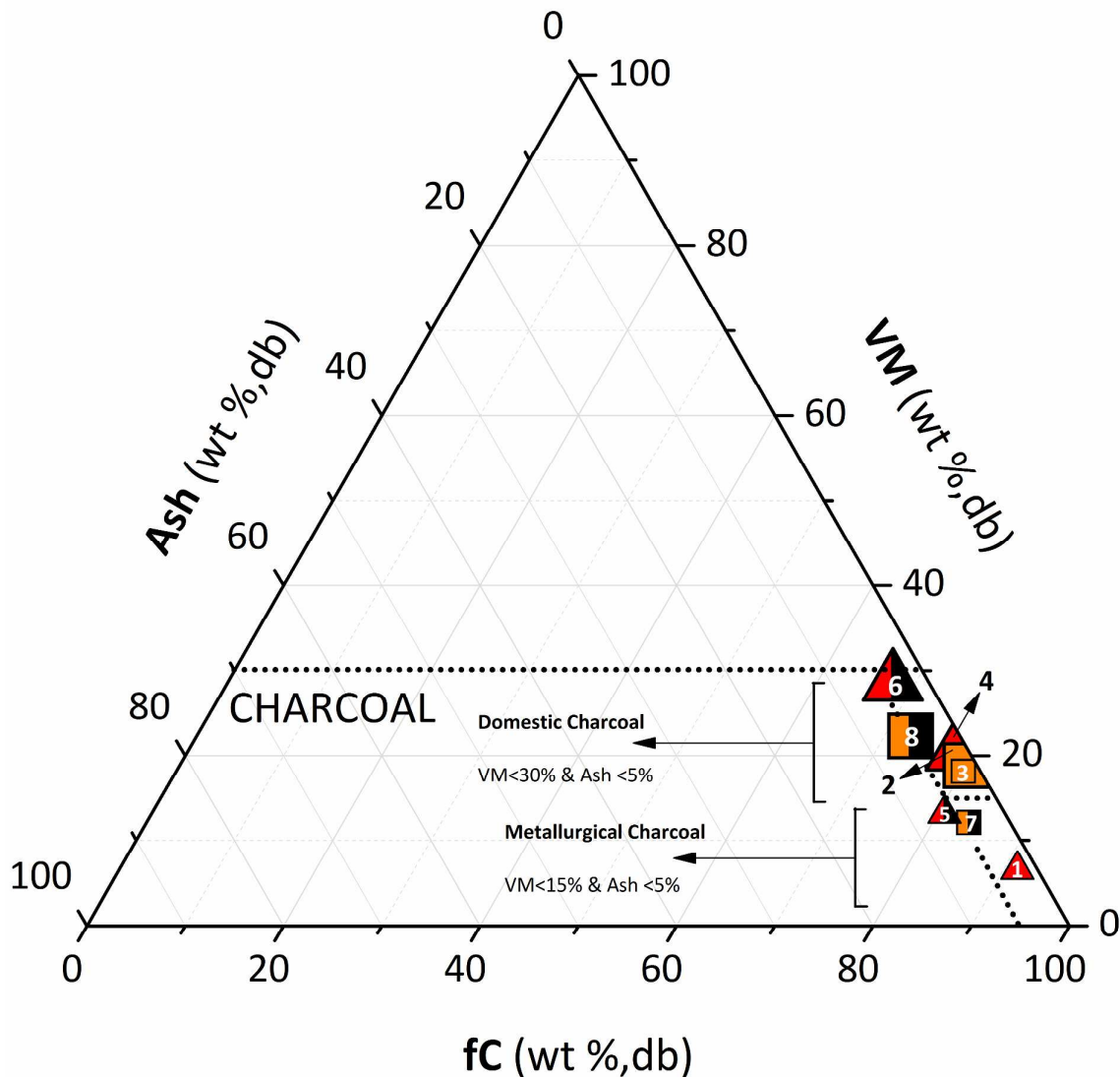content as a feed) produces a low ash containing charcoal.

Figure 4: Ternary plot to classify FC charcoal (made during FC experiments in Table 2) according to their fC, VM and Ash content (proximate analysis) . Birch and birch forest residue are presented by red and red/black triangles, respectively. Spruce and spruce forest residue are presented by orange and orange/black squares, respectively. Larger symbols show experiments done at 2.17 MPa, while smaller symbols designate experiments at 0.79 MPa.

Figure 5 compares the theoretical fixed carbon yields (found in Table 1) to the

experimental yields (see Table 3) and especially emphasizes the range of fixed-carbon yields

that can be obtained from Norwegian spruce, birch and their respective forest residues. It

shows that samples heated according to the conventional ASTM proximate analysis standards

(white symbols) realize the lowest experimental fixed carbon yields, with the exception of

birch forest residue. These proximate experiments were conducted in standard porcelain

crucibles with lid at 0.1 MPa atmospheric pressure. The flash carbonization results presented

in this paper show that increasing the reactor pressure from 0.79 MPa to 2.17 MPa, increases

the fixed carbon yields to up to 90% of the theoretical limiting value for birch and spruce

wood.

It is important to note that these equilibrium calculations provide insights into the

preferred products providing equilibrium has occurred in the reactor.
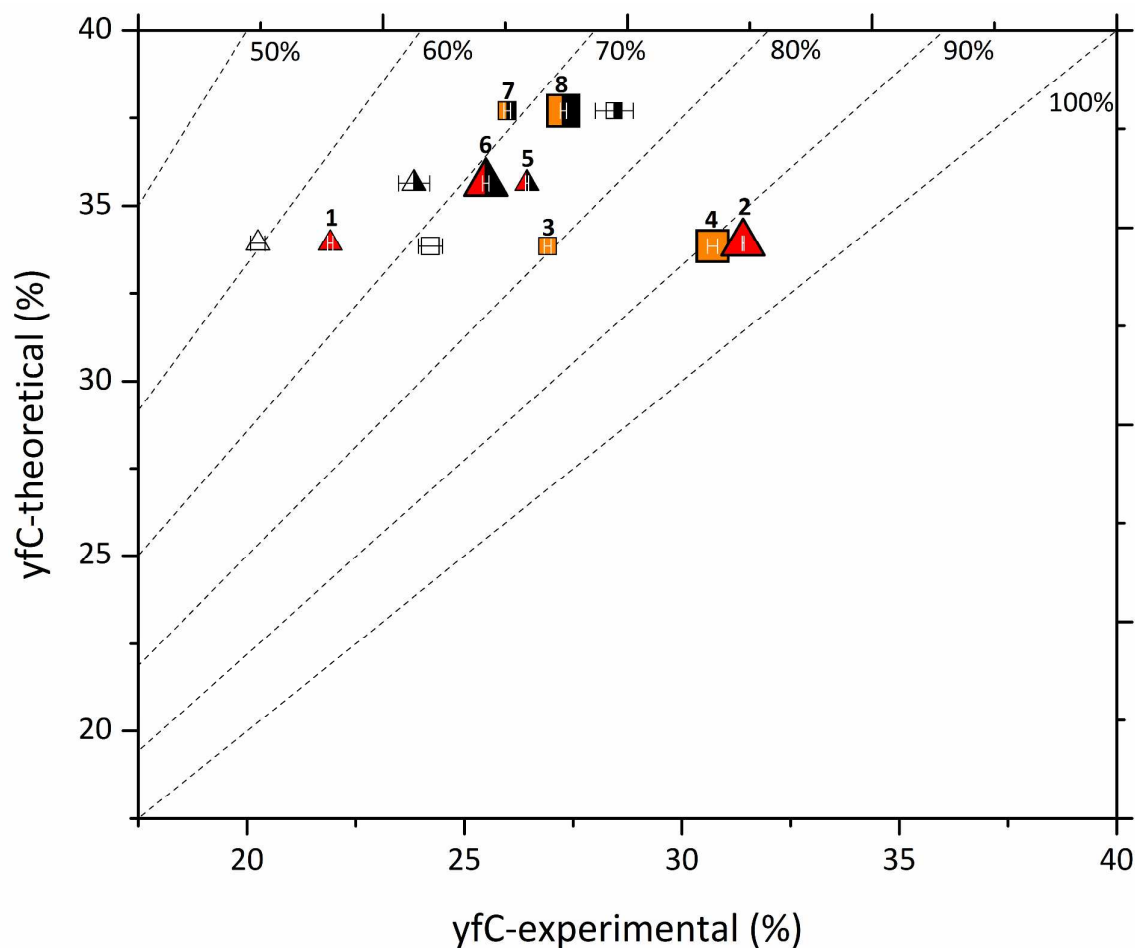
Figure 5: Parity plot displaying the experimental fixed carbon yields and their standard deviation error bars for the (numbered, See Table 3) FC experiments, versus the theoretical values calculated using the elemental analyses given in Table 1. Birch and birch forest residue are presented by red and red/black triangles, respectively. Spruce and spruce forest residue are presented by orange and orange/black squares, respectively. Larger symbols show experiments done at 2.17 MPa, while smaller symbols designate experiments at 0.79 MPa. The open symbols (triangles and squares) display the results of carbonizing birch, birch forest residue and spruce, spruce forest residue using the proximate analysis procedure at atmospheric conditions (see Table 1).
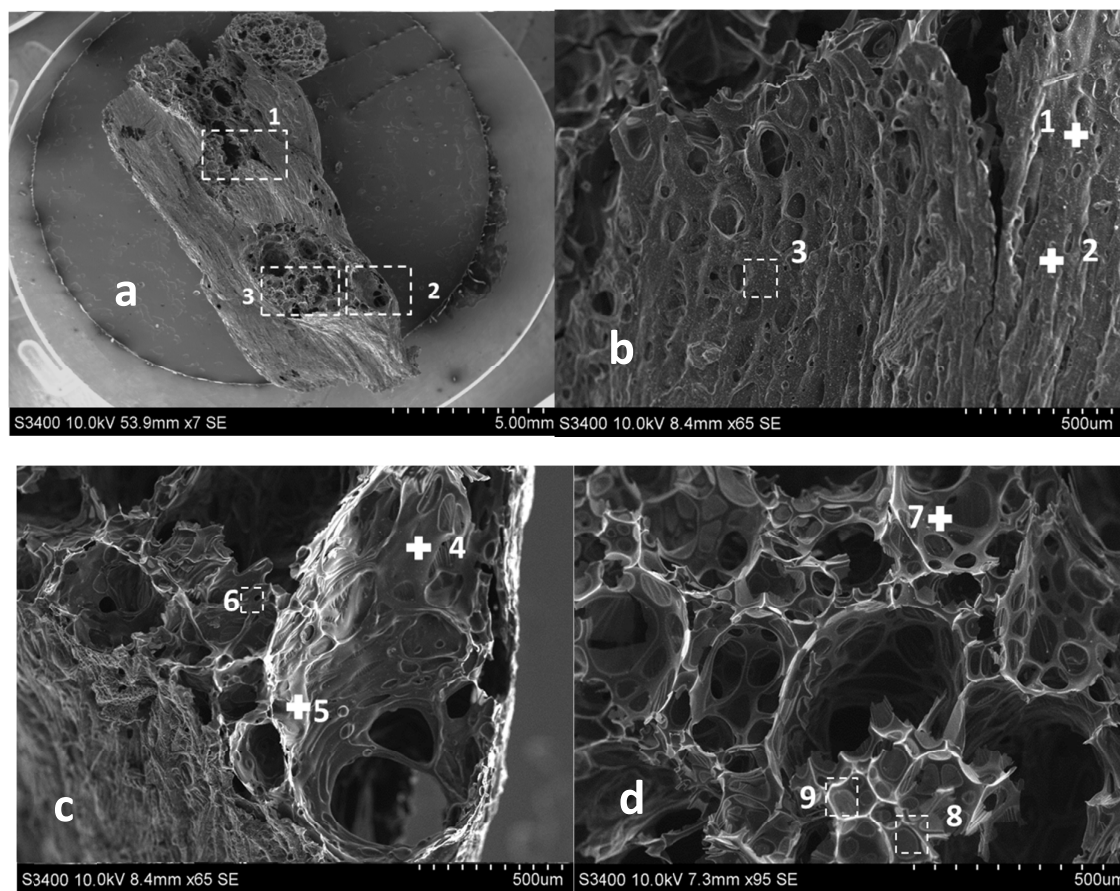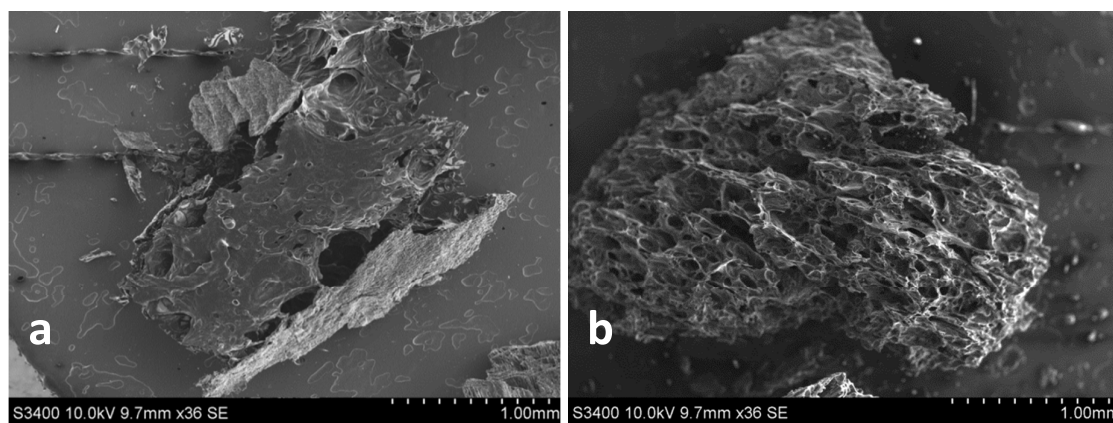
Figure 6: SEM images of fused birch wood charcoal produced under pressure of 2.17 MPa. (a) general view of a scanned fused birch wood char pieces. (b) close-ups of selected area 1 in (a). (c) close-up of selected area 2 in (a). (d) close-up of selected area 3 in (a)

**Table 5: EDX spot and area analyses on fused birch wood charcoal produced 2.17 MPa**

Element	spot 1	spot 2	area 3	spot 4	spot 5	area 6	spot 7	area 8	area 9
	Element composition in wt%								
C	74.5	72.78	73.92	87.07	84.59	88.19	90.74	80.79	88.15
O	24.64	26.57	25.41	12.36	13.95	10.62	3.65	3.71	3.88
K	0.37	0.27	0.24	0.31	0.35	0.46	2.12	3.31	3.01
Ca	0.41	0.26	0.33	NA	0.75	0.52	1.89	2.99	3.42
Ti	0.02	0.12	0.07	NA	NA	NA	0.02	NA	NA
Na	NA	NA	NA	NA	0.04	NA	0.02	NA	NA
Al	0.01	NA	NA	0.01	NA	NA	0.18	0.3	0.27
P	NA	NA	NA	NA	0.1	0.03	NA	0.4	0.37
S	NA	NA	NA	0.06	0.11	0.13	0.43	0.62	0.56
Co	NA	NA	0.03	0.15	0.03	NA	NA	NA	0.12
Zr	0.05	NA	NA	0.04	0.08	0.05	0.47	0.02	0.05
Ba	NA	NA	NA	NA	NA	NA	0.48	0.73	0.17
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

Figure 7: SEM images of birch wood charcoal produced under pressure of (a) 0.79 MPa and (b) 2.17 MPa.
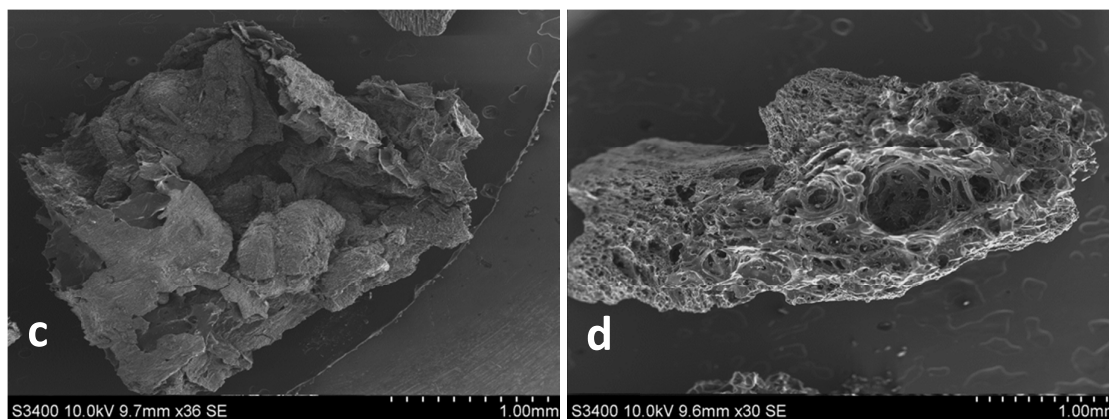
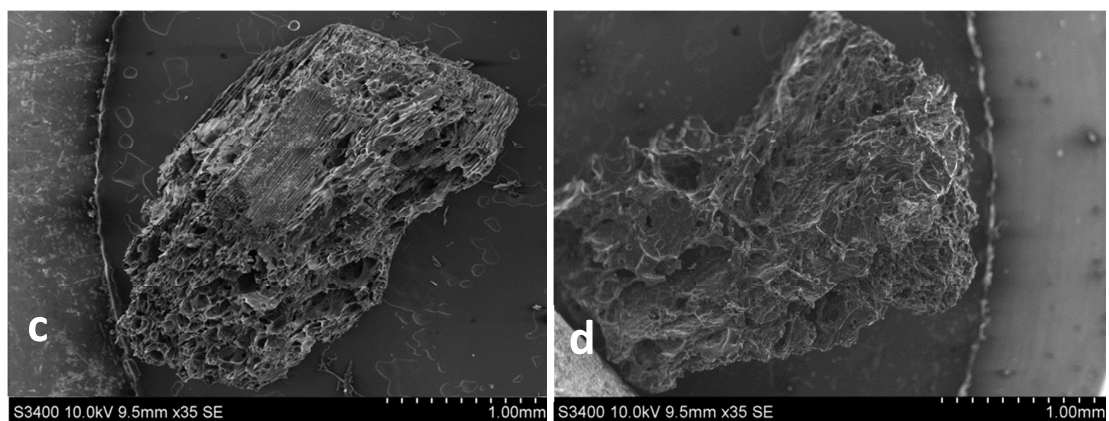**Figure 8: SEM images of birch forest residue charcoal produced under pressure of (a) 0.79 MPa and (b) 2.17 MPa.**
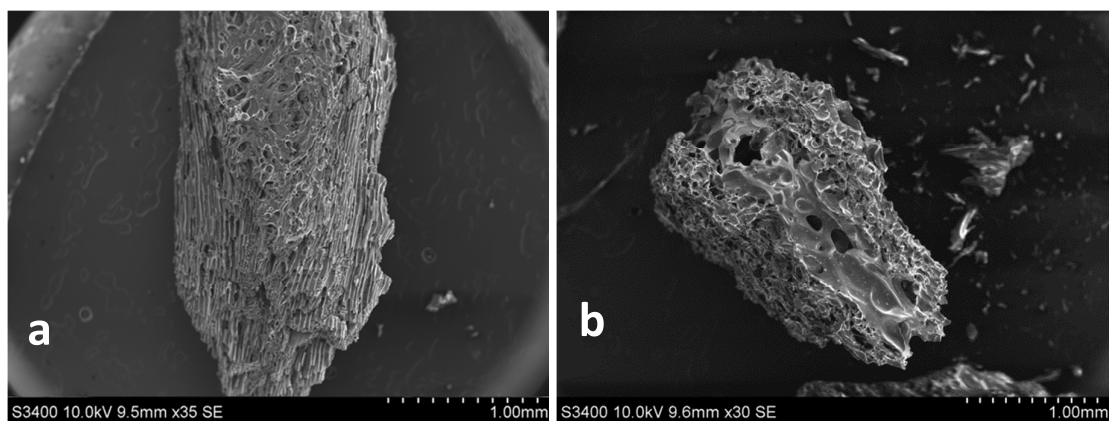
Figure 9: SEM images of spruce wood charcoal produced under pressure of (a) 0.79 MPa and (b) 2.17 MPa.

Figure 10: SEM images of spruce forest residue charcoal produced under pressure of (a) 0.79 MPa and (b) 2.17 MPa.

Figure 6 shows an SEM image of the fused birch wood charcoal particle from experiment 2.

The charcoal particle has an intact surface and does not show expected pores with the

exception of several evident large cavities. Several close-ups are made of Figure 6 (a) and displayed as b, c, and d. Figure 6 part b shows smooth surfaces of the particle and round openings of various sizes. It indicates intensive formation of melts and cenosphere on the charcoal particle surface. Part c shows a close-up of the spherical voids and the surrounding thin cell walls originating from the feed material. During the carbonization process, volatiles will generate inside the feed, which will cause the particles to swell because volatiles form inside the cell structure[55]. Because of these volatiles, the pressure inside the particles might be higher compared to the reactor pressure. Consequently, the volatiles will leave the particle and will cause the swelling particles to rupture. The SEM observations are in agreement with prior work[32, 55]

Semi-quantitative EDX analyses were also carried out for a microchemistry investigation of the fused birch wood charcoal particle of experiment number 2. The results of EDX analyses are summarized in Table 5. In general, spots and areas examined are rich in carbon with detection of oxygen and various inorganic elements. However, there are evident differences in terms of concentrations of elements detected from these spots and areas. Compared to the surface with mainly molten materials (Figure 6 (c), spot 1, 2 and area 3), the C content of the thin film (Figure 6(g), spot 7 and area 8, 9) is considerably high. In addition, the oxygen contents of the thin film are significantly low. The EDX analysis results suggest concentration differences of aromatic compounds (i.e., C-C and C-O bonds) in the different sampling spots and areas[56]. On the other hand, the concentration of Ca and K are evidently high in the thin film part of the particle. This creates suspicion that the thin film consists out of charcoal formed straight out of the biomass (primary char), while the molten part consists out of carbonized tars (secondary charcoal). It is well-known that some inorganic elements exist as ions in the biomass and are important for biological processes. These ions exist in both solid charcoal, intermediate liquid (i.e., molten phases and tarry vapors) and condensed phase and

act as catalyst to alter and direct the biomass pyrolysis chemistry [57, 58]. In brief, EDX analysis results indicate that a different part/section of a single fuel/charcoal particle might undergo different chemistry reactions.

Figure 7 and Figure 8 show SEM images of birch wood charcoal and its forest residue charcoals produced under pressures of 0.79 MPa and 2.17 MPa. Figure 7 shows the typical swelling phenomenon and partially melting of the birch wood and forest residue charcoal produced at 0.79 MPa. As shown in Figure 8, no obvious swelling can be observed from the charcoal particle produced at 2.17 MPa. However, the charcoal has passed through a severe melting stage, evidenced by glass like appearance.

Figure 9 and Figure 10 display SEM images of spruce and its forest residue charcoal. They show that part of the spruce and its forest residue charcoal has multicellular structure and cavities with different sizes. This structure and surface topography are similar to those raw biomass materials, which has been reported in previous studies[32, 55]. The images of the spruce and spruce FR charcoal particles made at 2.17 MPA have smoother and rather intact surfaces while no cell structure can be observed anymore. It indicates that the wood experienced a more intensive molten and resolidification stage.

Compared to charcoals produced from spruce wood and forest residue, swelling is more pronounced for the birch wood and its forest residue charcoals produced at 0.79 MPa. Additionally, more pores and voids can be observed from the birch wood and birch forest residue charcoal produced under pressures of 2.17 MPa. The birch wood and forest residues contain higher levels of volatile matter, in comparison to spruce wood and forest residue. Release of volatile matter from birch wood and forest residue particles might be more intensive, resulting in an evident expansion of fuel particles and formation of large voids.

4. Conclusions

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 is being used.

2. The results of the forest residue carbonization experiments are promising. Feeds that are very heterogeneous in texture such as forest residue 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 forest residue 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.

4. An increase from 0.79 MPa to 2.17 MPa, increases the fixed carbon yields to over 90% of the theoretical fixed carbon yield for both birch and spruce wood. For the forest residues, values over 80% can be attained. Both results show that the flash carbonization technique can provide serious cost-savings to the Norwegian metallurgical industry and prevent excessive deforestation. The use of coal has been waning, and the introduction of high yield charcoal might be the final blow.

5. The in-dept analysis using SEM allowed us to differentiate between 'molten' char or secondary char and primary char. The original feed morphology is not visible in charcoals produced at 2.17 MPa because of intense and fast devolatalization.

6. Dr. Michael Jerry Antal nurtured the Flash Carbonization technique and allowed students of the R^3-laboratory to upgrade the apparatus with the latest state of the art tools. Dr. Antal always advocated to use the proximate analysis as a ranking tool for charcoals because of its widespread use. The fixed carbon yield of his high pressure charcoals was what Dr. Antal liked to brag about most. "Bon voyage", Dr. Antal.

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