Carbonization pressure influence on fixed carbon yield

Øyvind Skreiberg*[a], Liang Wang[a], Quang-Vu Bach[b], Morten Grønli[c]

[a]SINTEF Energy Research, Postboks 4761 Torgarden, 7465 Trondheim, Norway
[b]School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul, Republic of Korea
[c]Department of Energy and Process Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway
*oyvind.skreiberg@sintef.no

Biocarbon, or charcoal, is receiving increased attention as an increasingly important reductant in metallurgical industries, and has as well many others uses, e.g. as high quality fuel or as activated carbon. Traditional charcoal production processes are very inefficient, giving charcoal with low fixed carbon yields. A number of parameters influence the yield, including feedstock properties and carbonization process conditions. The importance of temperature is rather well known. However, the influence of pressure is more debated, and many parameters may influence the carbonization process simultaneously, making it hard to establish the real influence of pressure. In this work, based on thermodynamics and kinetics evaluations, and through comparison with experiments at atmospheric and pressurised conditions, the influence of pressure is presented and evaluated, as a function of temperature and choice of carrier gas, as well as feedstock properties. Possibilities for atmospheric carbonization systems to approach the performance of pressurised systems are discussed. Comparison with wet pressurised carbonization systems is made. Finally, recommendations for improved carbonization process conditions are given.

1. Introduction

Biocarbon (or charcoal) has many uses, for energy production, as a reductant in metallurgical processes, for soil amendment, as active carbon etc. The produced biocarbon will have a set of properties and a certain quality, a quality that depends on its intended end use. Several carbonization process indicators have been proposed (Antal, 2003). The **biocarbon yield** (mass of dry biocarbon vs mass of dry biomass) depends on a number of feedstock properties and carbonization process parameters, and is not a measure of quality. For use in metallurgical processes, the **fixed carbon content** (% fixed carbon in the dry biocarbon) is essential, but depending on the metallurgical process, a number of other biocarbon properties are important, even crucial. From an economical point of view the **fixed carbon yield** (mass of fixed carbon vs mass of dry ash free biomass) should be essential, while fixed carbon content is not a measure of carbonization process performance. Approaching the **theoretical fixed carbon yield** (which can be established through an equilibrium calculation) is wanted, i.e. maximising it by optimising the carbonization process parameters and feedstock properties. The fixed carbon yield of atmospheric carbonization processes today is rather low compared to the theoretical fixed carbon yield, while pressurised carbonization processes approach the theoretical yield. It is then very interesting to know the real effect of an increased pressure, and if atmospheric carbonization processes could be significantly improved.

2. Influencing parameters on the fixed carbon yield

A number of different feedstock and process parameters influence the fixed carbon yield of a carbonization process, where a solid feedstock is heated in an inert or oxygen starved atmosphere, releasing volatiles to produce a biocarbon enriched in carbon. Influencing process parameters are temperature, residence time, "inert" gas flow rate or amount, heating rate, pressure and the carbonization reactor type/configuration. Influencing feedstock parameters are moisture content, physical properties, e.g. particle size, chemical

properties, e.g. lignin content, elemental composition, especially carbon, ash amount and composition, e.g. catalytic elements. However, the question is why and to what extent these parameters influence. With all these influencing factors it might seem rather complex, however, maybe it is much simpler than it looks?

2.1 What is theoretically achievable?

What's theoretically achievable with respect to fixed carbon yield can be assessed by carrying out multi-phase equilibrium calculations, i.e. assuming infinite residence time. Hence, this makes it possible to distinguish between the individual effects of other parameters, like pressure, temperature and biomass composition. Interesting aspects are e.g. 1) the fixed carbon yield as a function of the biomass carbon content, 2) the influence of the hydrogen and oxygen content in the biomass, 3) the influence of the choice of carrier gas composition and amount (e.g. inert, CO_2, H_2O), 4) the influence of pressure, and 5) the influence of temperature. In this work STANJAN (Reynolds, 1987) has been used to carry out constant temperature and pressure equilibrium calculations, minimising Gibbs free energy, to investigate this for mixtures of elements corresponding to the combined fuel and carrier gas composition, and including all relevant gas species in the equilibrium product, as well as solid C and liquid H_2O in separate phases.

2.2 The effect of biomass composition

The main elements in the biomass are C, H and O. Minor elements like N, S and Cl will also be present, but in usually relatively small amounts, and they will as well form gases that do not directly contribute to fixed carbon consumption, only to a minor gas phase dilution. Additionally, ash elements are present, whereof some of them also have catalytic effects when it comes to cracking tars, which benefit an increased fixed carbon yield in a real carbonisation process with residence time limitations, or rather a faster route towards the equilibrium condition. However, in this work we will assume that the base case biomass only consists of C (50.94 wt%), H (6.05 wt%), O (42.95 wt%) and N (0.06 wt%, minor amount).

Obviously, the fixed carbon yield will increase with increasing carbon content. However, one interesting question is if, at otherwise constant conditions, the **normalised fixed carbon yield** (mass of fixed carbon vs mass of feedstock carbon) actually changes similarly with changing carbon content. To investigate this, a set of equilibrium calculations was carried out at constant temperature and pressure, for a range of temperatures and at pressures. The carbon content was increased by decreasing the H, O and N content with a same percentage. As shown in Figure 1 for a temperature of 673 K, the fixed carbon yield (Yfc) do indeed increase with increasing carbon content in the biomass, at a close to linear rate, but the normalised fixed carbon yield (NYfc) increases with a non-linear rate. Hence, the amount of H and O in the biomass, through formed gas species from these, do contribute to fixed carbon consumption, and not only to a different amount of permanent gases, and the rate of consumption increases with decreasing carbon content. The effect of pressure is here (at 673 K) minor, and actually a slightly higher fixed carbon yield is reached at 1 atm compared to 10 atm.
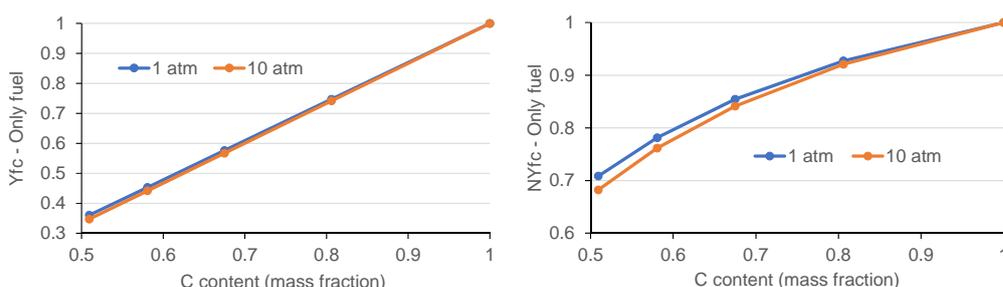
Figure 1: Fixed carbon yield and normalized fixed carbon yield, as a function of carbon content in the biomass, at a temperature of 673 K and at a pressure of 1 and 10 atm.

If keeping the mass fraction of carbon and nitrogen constant (Base case: 50.94 wt% C; O/H ratio of 7.1) while changing the mass ratio between oxygen and hydrogen (O/H) and plotting the normalised fixed carbon yield (Figure 2) as a function of temperature for the same two pressures, the effect of the H and O in the feedstock is revealed. Unless the O/H ratio is very low, giving a high H content and a high equilibrium concentration of CH_4, the influence of the O/H ratio is not very large at lower temperatures (below 773 K). However, at higher temperatures the situation changes, as the concentration of CH_4 decreases and the hydrogen goes to H_2 and H_2O instead. Then a low O content is beneficial as less gasification agents (H_2O, and CO_2) will be formed. Hence, the fixed carbon yield increases. The effect of pressure is that at very low temperature H_2O is also present in liquid form, removing H and O to the liquid phase, and also that a wider temperature range with a relatively high fixed carbon yield exists. However, in this temperature range the effect of pressure seems minor.

In Figure 3 the normalised fixed carbon yield is shown as a function of temperature and pressure (1 to 50 atm) at two O/H ratios (7.1 and 12.24). As pressure increases, more H_2O will be in liquid form at very low temperatures. As temperature increases there is a quite wide temperature range where the pressure hardly influences the fixed carbon yield, until reaching a high enough temperature for fixed carbon gasification by H_2O and CO_2. If increasing the O/H ratio from 7.1 in the base case to 12.24 the temperature range where the fixed carbon yield is not influenced by the pressure becomes narrower, however the fixed carbon yield increases somewhat.
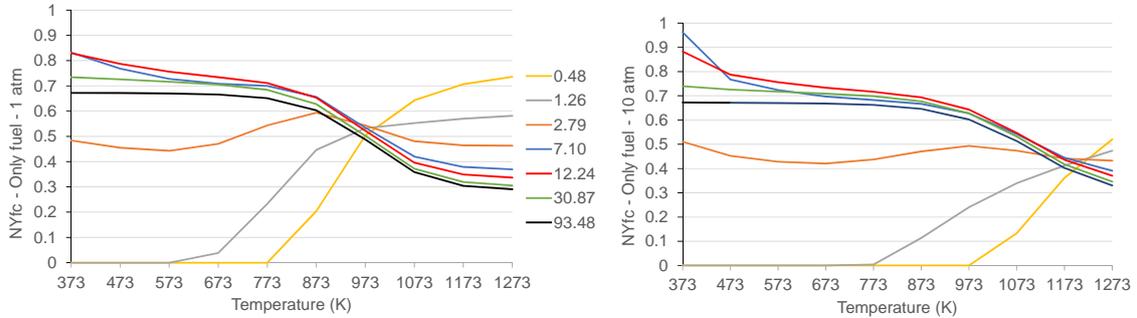
Figure 2: Normalised fixed carbon yield as a function of temperature and O/H ratio (0.48-93.48) for a constant carbon content in the feedstock, at a pressure of 1 and 10 atm.
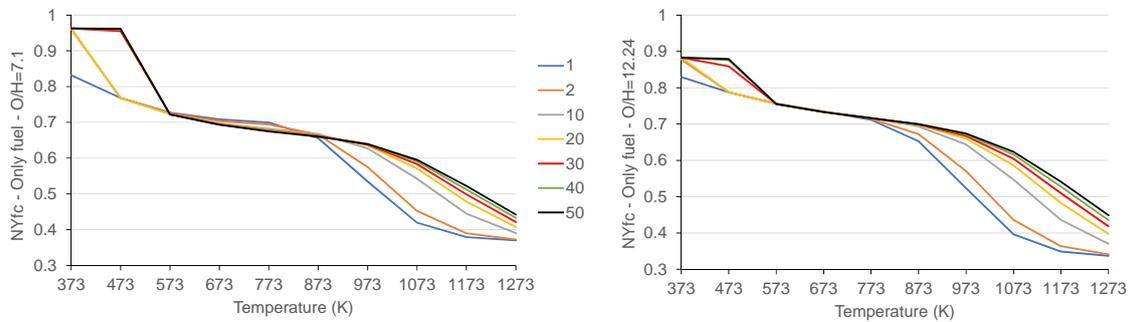
Figure 3: Normalised fixed carbon yield as a function of temperature and pressure (1-50 atm) for a constant carbon content in the feedstock, at an O/H ratio of 7.1 and 12.24.

2.3 The effect of carrier gas composition and amount

Typically inert gas (N_2) is used as carrier gas. The question becomes if the amount of inert gas is of any importance at equilibrium conditions. As shown in Figure 4, the answer is no significant importance until reaching char gasification temperatures, as the gas phase dilution by N_2 mainly just means that longer residence time is needed to reach the equilibrium condition. When reaching char gasification temperatures, the inert N_2 that reduces the partial pressure of CO_2, gives a reduced fixed carbon yield. This is due to a shift in the equilibrium condition, moving more of the carbon into the gas phase to compensate for the dilution effect. If using CO_2 as carrier gas the equilibrium is shifted in the other direction, increasing the fixed carbon yield until reaching char gasification temperatures, where after the CO_2 will gasify the fixed carbon. For both N_2 and CO_2 as carrier gas, a reduced carrier gas amount reduces as expected the influence of the carrier gas on the equilibrium condition. If water vapour as another gasification agent is used instead of CO_2, this will start gasifying the fixed carbon at significantly lower temperatures compared to CO_2, and decrease the fixed carbon yield accordingly. If moisture is present in the biomass, this would have such an effect.
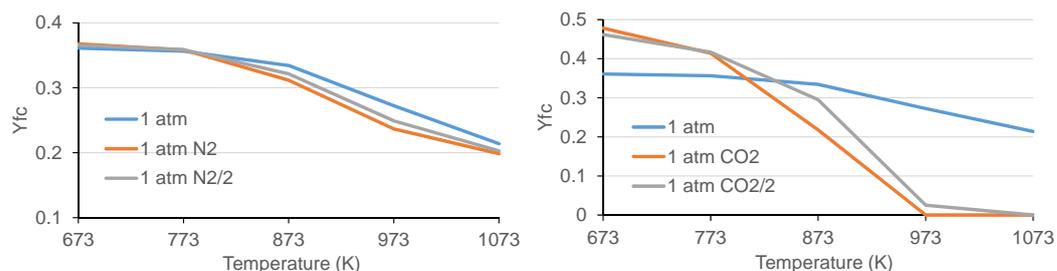
Figure 4: Fixed carbon yield as a function of temperature and carrier gas choice and amount (1 atm: no carrier gas, N_2 or CO_2: carrier gas addition, N_2/2 and CO_2/2: halved molar addition of N_2 or CO_2) at a pressure of 1 atm.

When adding a carrier gas in the equilibrium calculation this in practise means a change in the "feedstock" composition, i.e. adding inert N_2 will only cause dilution, while adding CO_2 will increase the C content, but also the O content.

2.4 The effect of pressure at constant pressure
The effect of pressure has already partly been revealed in Figures 1 to 3. In addition Figure 5 compares directly the pressure influence on the fixed carbon yield as a function of temperature, with and without N_2 as carrier gas.
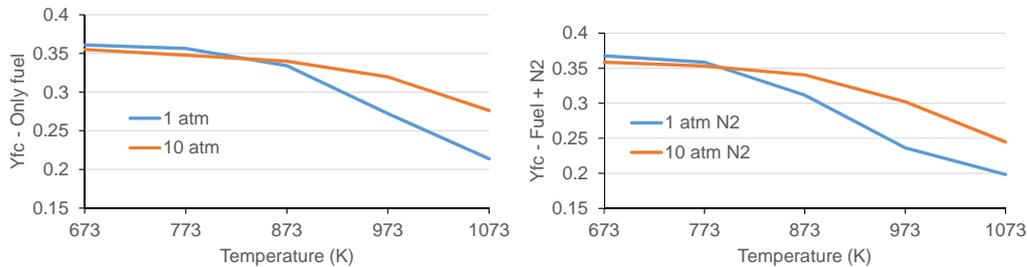
Figure 5: Fixed carbon yield as a function of temperature and pressure, with and without inert carrier gas.

Le Chatelier's principle implies that increasing pressure will seek to reduce the overall molar concentration, i.e. favour CO_2, H_2O and CH_4 on the expense of H_2 and CO as shown in Figure 6. Hence, increased fixed carbon yields results at higher temperatures as shown in Figure 5. The somewhat lower fixed carbon yield at 10 atmosphere pressure at lower temperatures is caused by the methanation reaction ($C+2H_2 > CH_4$) which is favoured at low temperature and high pressure, contrary to the Boudouard reaction ($CO_2+C > 2CO$) and the water gas reaction ($H_2O+C > H_2+CO$) that are favoured at high temperature and low pressure. However, even at atmospheric pressure there is a slight effect of the methanation reaction at lower temperatures. Also, with increased pressure the equilibrium condition is reached faster, as a result of increased partial pressures. For practical applications the reaction rates of these reactions become important, and then the methanation reaction can be neglected as it is very slow, while operating at higher temperatures will be possible without detrimental effects on the fixed carbon yield due to fixed carbon gasification, as the residence time is not infinite.
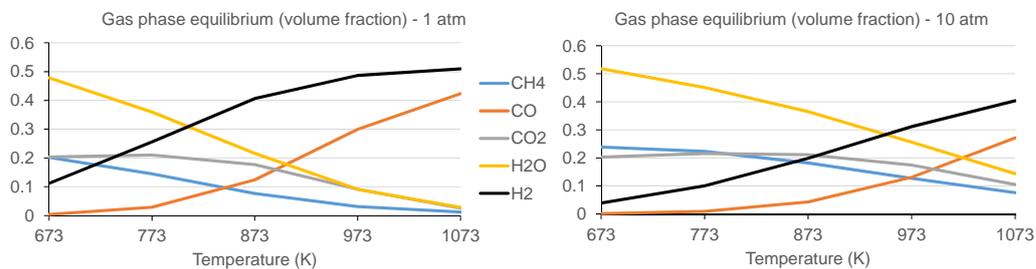
Figure 6: Gas phase equilibrium concentration as a function of temperature, at a pressure of 1 and 10 atm.

2.5 The effect of pressure at constant volume
The effect of applying constant volume conditions (constant T, V), i.e. another reactor configuration, is at equilibrium conditions only a pressure effect. By applying an initial pressure and a temperature, the pressure has to increase at constant volume conditions. If adjusting the volume to a volume that will give a specific pressure, the results will be identical to that of a constant (T, P) calculation at that pressure. The potential benefit of a constant volume condition lies in the self-induced system pressure increase, even reaching a pressure where H_2O partly will be present in liquid form. As for constant pressure conditions, the amount of "carrier" gas vs the amount of biomass to be carbonised is of some importance. This can in practise be adjusted by adjusting the biomass loading in a constant volume reactor, which will also influence the pressure that can be reached.
The effect of reaching a pressure high enough to give H_2O in liquid phase is that the H_2O is taken out of the gas phase. This gives a positive effect on the fixed carbon yield, as the effect is similar to that of increased carbon content in the biomass. I.e. removing a corresponding amount of H and O from the biomass, and thereby from the gas phase. As at constant temperature and pressure conditions, there will be an optimum O/H ratio in the biomass that leads to a maximised fixed carbon yield.

2.6 The effect of pressure with a liquid phase carrier medium
Wet carbonisation is a process where the "carrier" medium is hot compressed liquid water, i.e. the biomass is completely submerged into the water. This creates a completely different starting condition compared to starting

with biomass and a carrier gas. This results in an insignificant effect of pressure as long as the pressure is high enough to ensure that all the H_2O, including that formed from the H and O in the biomass, is in liquid form. As the biomass is completely submerged into the water, the influence of a particle exterior gas phase and the possibility of influencing the fixed carbon yield through the gas phase are not present. Additionally, the biomass when submerged becomes saturated or partly saturated with water, which may negatively influence the fixed carbon yield through reduced particle interior secondary char forming potential.

3. Comparison with experimental fixed carbon yields

Through the years a large number of publications have investigated achievable fixed carbon yields in different types of reactors at different process conditions and for different kinds of biomass feedstocks. In some of these comparison with a theoretical fixed carbon yield is made, visualised e.g. in parity plots. The influence of pressure has also been investigated, at both constant pressure and constant volume conditions.

Figure 7 presents experimental results from selected works using different kinds of reactors. High fixed carbon yields are usually achieved at pressurised conditions, with on average the highest yields achieved at constant volume conditions, i.e. conditions that can be expected to get closest to equilibrium conditions. However, there are significant variations that are due to other influencing factors than pressure and C content.
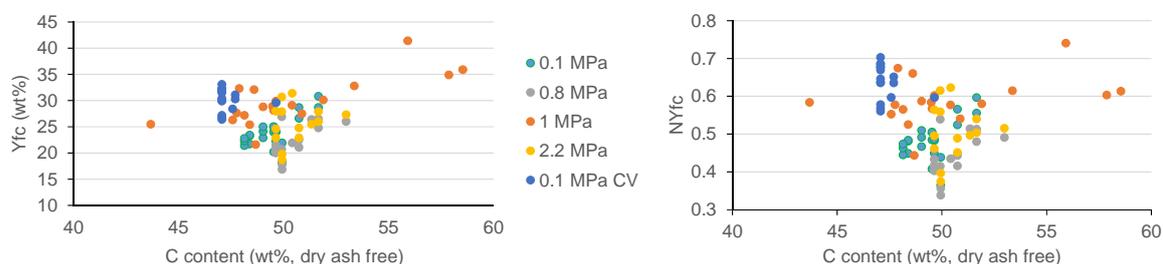
Figure 7: Experimentally achieved fixed carbon yields as a function of C content and pressure (CV: constant volume reactor, initial pressure) (Antal, 2000; Wang, 2016; Van Wesenbeeck, 2016; Legarra, 2018).

4. Discussions

When talking about the fixed carbon content as given by a proximate analysis one should keep in mind that it is not only fixed carbon, as there always will be a certain amount of oxygen, hydrogen and minor non-ash elements bound in the char matrix. I.e. experimentally achieved fixed carbon yields might be somewhat overestimated. The pressure is not a directly influencing carbonization process parameter, as there are no influential pressure dependent gas phase reactions (referring to classical gas phase reaction kinetics and 3rd body reactions). However, the pressure will increase the partial pressure of gas phase reactants, and a change in pressure influences the thermodynamic equilibrium conditions as well, in accordance with Le Chatelier's principle. Also, increased system pressure increases the residence time inside (and outside) the char matrix, and there is a potential for a significant additional pressure build-up inside a particle, a potential which influence increases with increasing particle size. In reality, atmospheric carbonization processes, or rather process conditions, hardly exist in practise. Secondary tar cracking reactions to form permanent gases and secondary char can have lower activation energies and pre-exponential factors than for the formation of permanent gases, tar and primary char, i.e. not very temperature dependent, but residence time dependent. Fixed carbon yield increase through secondary char formation is a heterogeneous process, i.e. physical contact between tarry vapours and the char matrix is required, to enable repolymerisation and chemical bonding of the secondary char. As shown in this work, temperature itself is maybe not very important (up to a certain temperature, where char gasification reactions become important), while residence time might be crucial. Hence, for a maximised fixed carbon yield then it is primarily about maximising residence time and char matrix interaction.

Loss of fixed carbon compared to the theoretical yield is due to release of tarry vapours into an atmosphere which cannot again come in contact with the char matrix. In the extreme case of flash pyrolysis, these vapours are very fast released from typically small particles, without chance of contributing to secondary char formation, leaving behind a low fixed carbon yield. Oppositely, carbonisation processes employ typically slow pyrolysis (low heating rate). This alone raises the fixed carbon yield significantly for the same small particles. However, typically, still the yield is far from the theoretical yield. To exploit the full fixed carbon yield potential, additional process parameters must be optimised, to utilise the full potential of the tarry vapours, i.e. cracking them simply put to one part permanent gases and one part fixed carbon. From the above considerations it becomes obvious that the process conditions at which the theoretical fixed carbon yield is calculated becomes important, in addition to the elemental composition of the feedstock. The usual approach would be to carry out the calculation

with the feedstock CHON elemental composition at a selected "representative" temperature and pressure. As process conditions do influence the achievable fixed carbon yield the calculation should be carried out at the same process conditions as the experimentally derived yield. However, the equilibrium will in practise never be reached, but all parameters that speed up reaction rates and increases the residence time will contribute to getting closer to the equilibrium condition. Pressure affects residence time as well as concentrations. Higher pressure increases the residence time inside a particle. Higher pressure increases the tarry vapour concentrations inside the particle, which means higher reaction rates. Also, increasing particle size increases the residence time inside the particle, and has the potential to additionally increase the pressure influence inside the particle. Permeability is then a key factor. Higher pressure at constant volume conditions removes the need for large particles, as outflowing tar eventually will come in contact with the char matrix through the large outer surface area of the many small particles. Is it possible to achieve almost the same at "atmospheric" pressure? In theory: Yes, if you can achieve the same residence time without degrading of the tars' potential to form secondary char. In practise: No, as gas/tar confinement and recirculation approaches have practical limitations.

5. Conclusions

In this work equilibrium calculations have been carried out to investigate the effect of feedstock and process conditions on the achievable fixed carbon yield, i.e. the theoretical fixed carbon yield. Temperature is an influencing process parameter, but at typical carbonization reactor temperatures (673-873 K) the influence is small. The effect of pressure is primarily through Le Chatelier's principle, with an increasing pressure extending the temperature range with high fixed carbon yield somewhat. The effect of a carrier gas is as a feedstock diluent only in the case of N_2 and as additional reactant in the case of CO_2. The effect of feedstock composition is both through the carbon content itself, and through the O/H ratio. An optimum O/H ratio exists, giving the highest fixed carbon yield. At high pressure, e.g. if applying constant volume conditions, removal of H_2O from the gas phase to a liquid phase will increase the fixed carbon yield, and the effect is similar to increasing the feedstock carbon content. Other influencing factors that have been found in practise, like heating rate, particle size and residence time, are primarily influencing the contact time between tarry vapours and the char matrix. With respect to residence time effects, the pressure becomes very important, and this is the most important pressure effect. An increased pressure makes it possible to approach the theoretical fixed carbon yield much faster, through increased contact time between tarry vapours and the char matrix, as well as through increased partial pressures. Hence, reaction rates and extents increase. A constant volume reactor has the potential to get closest to the theoretical fixed carbon yield, through high pressures and keeping all the tarry vapours inside the reactor for the time needed for all of them to finally react. In such a case feedstock physical properties such as particle size become less important. If fixed carbon yield was the only important criteria, pressurised carbonization is the solution, due to the much increased secondary char formation potential. Considering the increased complexity and cost of pressurized systems, the overall benefit is not so clear. However, there is a certain potential in optimizing "atmospheric" carbonization processes, i.e. do everything you can to increase residence time: large particles, low heating rate, reducing the inert gas flow rate, volatiles confinement and recirculation and optimising the potential for released volatiles to react at the surface of or inside other particles.
It's rather simple, if you apply a high enough temperature, but not more, then it is "all" about residence time.

References

Antal M.J., Allen S.G., Dai X., Shimizu B., Tam M.S., Grønli M., 2000, Attainment of the Theoretical Yield of Carbon from Biomass, Ind. Eng. Chem. Res., 39(11), 4024-4031.

Antal M.J., Grønli M., 2003, The Art, Science, and Technology of Charcoal Production, Ind. Eng. Chem. Res., 42, 1619-1640.

Legarra M., Morgan T., Turn S., Wang L., Skreiberg Ø., Antal Jr. M.J., Carbonization of biomass in constant-volume reactors, Energy & Fuels, 32(1), 475-489.

Reynolds W.C., 1987, STANJAN Thermochemical Equilibrium Software, version 3.91, Stanford University: Stanford, CA.

Van Wesenbeeck S., Wang L., Ronsse F., Prins W., Skreiberg Ø., Antal Jr. M.J., 2016, Charcoal 'mines' in the Norwegian woods, Energy & Fuels, 30(10), 7959-7970.

Wang L., Skreiberg Ø., Van Wesenbeeck S., Grønli M., Antal Jr. M.J., 2016, Experimental Study on Charcoal Production from Woody Biomass, Energy & Fuels, 30(10), 7994-8008.