# Smelting Science

1. Furnace and Fire

Fire

For a long time the only way to make something hot was to burn some organic matter. Until the Middle Ages this was pretty much the remains of recently diseased organisms - wood, straw, dung. Burning the remains of organisms that died a *long* time ago like oil, coal, or peat was rarely done in the old times.
Some sophistication comes only from using charcoal instead of wood, i.e. *processed* or concentrated fuel. I'll get to that, here we only work with unprocessed (if dried) bio-fuels, essentially **wood**.
First let's look very generally at what happens when a solid piece of something burns.

- Oxygen molecules (O_2) from the air react with the carbon at the *surface* of the burning piece of material, forming CO_2. Starting the reaction needs a certain amount of energy, and that's why you have to light a fire. However, whence the reaction starts, a lot of energy is released so that the balance is positive - forming CO_2 releases more energy than needed to start the process. The net energy released is transferred to the various molecules around. The gas molecules then simply speed up compared to their average speed at room temperature.

Fire!!!
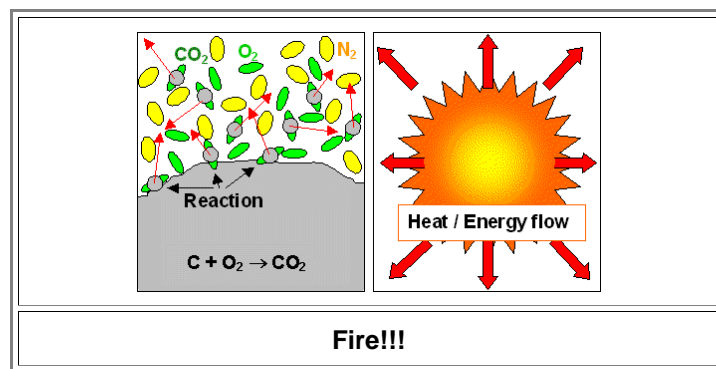
- Reactions can only happen at the surface. The energy generated flows out in all directions, very schematically indicated by the red arrows on the the CO_2 molecules. Arrows indicating the velocity of the "cold" oxygen and nitrogen molecules would be too short to be visible on this scale.
The energy from the chemical reaction we call "burning", "fire", or "oxidation" flows out in all directions since the "hot" molecules move about and away. It gets diluted since the "hot" gas molecules transfer energy to the "cold" ones they encounter, or to whatever else they hit, for example the atoms / molecules in the wall of some enclosure. Their energy decays from "hot" to "ambient", and we know how that goes from beer science

This is an exceedingly simple but perfectly correct way to visualize "fire" on the atomic scale - the only scale that counts! It allows to draw some rather far-reaching conclusions:

- **1.** When something burns there is always a **maximum temperature T_{max}** that can be achieved. Temperature, as we know, is just another word for "average energy contained in the *random* movement of elementary things like atoms or molecules". The energy gained by the "burning" reaction, e.g. **C + O_2 ⇒ CO_2 + energy**, is transferred to the atoms and molecules involved (including innocent bystanders like the nitrogen molecules of the air or the water molecules contained in the wood) - and that's it. The molecules and atoms involved contain now more energy and are thus "hotter" - but only by a certain amount that one can calculate.
Burning pure carbon in air at best gives you $T_{max} \approx$ **2000 ⁰C (3600 ⁰F)**. Burning acetylene (**C_2H_5**) with pure oxygen gives you more energy and thus a higher T_{max} - you can use that for welding or cutting steel. Well-dried hardwood contains around 50 % carbon and gives a $T_{max} \approx$ **1600 ⁰C (2912 ⁰F)**.

- **2.** The energy production in your fire, or how much energy is produced *per second* (called "power"), is given by how much reactions of the type **C + O_2 ⇒ CO_2 + energy** take place *per second*.
This is obviously controlled by:

    - The total surface area accessible. The burning reaction, after all, can only occur at the surface of something solid. That's why a number of small pieces of fuel produce more heat than just one solid lump of the same weight: they provide more surface area.
    - The supply of oxygen. That's why blowing air on the burning surface, or through your bed of "coal" lumps, makes for more heat energy production. It does *not* raise the *maximum* temperature T_{max}, however.

- **3.** Heat energy cannot be fully contained in a given space. It always flows out. This is special. The energy contained in the fuel before you burn it stays where it is, just as the energy in a tensed spring and so on. But heat energy *always* flows out from wherever it was produced, and this dilutes the energy / velocity contained in the molecules, lowering the temperature with increasing distance from the energy source. All you can do is to minimize the heat

flow by "damming" it, by putting materials with low heat conductivity in its way. There is always some leakage, however.

A fire in an open hearth rapidly distributes the energy produced in all directions; the temperature thus goes down rapidly with distance. That's why you need to suppress these losses by building a container around the fire in your hearth. And now we are talking *furnaces* or *kilns*.

<h3 style="text-align:center; color:red">First Insight into Furnace Operation and Design</h3>

Putting this insights together with a tiny little bit of math, we arrive at some very simple but far reaching equations / conclusions:

● **1.** The **temperature** T at any given place in your **furnace** or kiln is determined by how much energy or "heat" flows into it (let's denote that by H_{in}) in relation to how much energy flows out of it and is lost; H_{out}. The temperature you will get then is

$$T = T_{max} (1 - H_{out}/H_{in})$$

Let's look at a simple example: If your energy influx is H_{in} = **100 kJ/s**, and you loose **10 %**, i.e. the outflux is H_{out} = **10 kJ/s**, your temperature is $T = T_{max}(1 - 0.1) = 0.9\ T_{max}$. Instead of, for example, **2 000 ºC**, you only have **1 800 ºC**. Note that a loss of only 10 % is very small; you typically must reckon to have far higher values. Energy losses contain not only the energy flowing through the furnace wall but also the hot gases escaping through the flue and all the heat needed to heat up the furnace itself (at least the inside lining is hot) and the charge.

● **2.** The **energy** produced comes from a bed of burning **fuel**, e.g. charcoal or wood, that occupies a certain *volume*. The energy production then is proportional to that volume; at least in some approximation.

You contain your burning fuel in a "container" like the typical cylindrical tube of a bloomery smelting furnace. The energy flowing out must go through the internal *surface* of this container - the walls of the tube, the opening at the top, the bottom. The ratio of energy produced to energy flowing out thus gets better for big furnaces - they have a smaller surface to volume ratio. You are also wasting less energy for heating up your container. This is old stuff we considered this at length before, just for a different purpose. So big furnaces would be better than smaller ones? Yes, there is substantial "economy of size" - but there is also a catch:

● **3. Air supply**. As mentioned above, the amount of air/ oxygen you supply determines the production rate of heat energy, together with the amount of reactive fuel surface provided. If you want high temperatures you must supply heat energy far more quickly then it can leak out, and that means that you must supply sufficient air.

The decisive quantity "**air flow**" AF is measured by how many cubic meters of air are run through the contraption per square meter and second. That gives as measuring unit $[AF] = m^3/m^2 \cdot s = m/s$, i.e. the unit of a *velocity*. That's why everybody in the business talks about the air **space velocity** inside a furnace. However, a space velocity of, e.g., **1 m/s** does *not* mean that the air actually flows with that velocity through your furnace even so that velocity would supply the right amount of air. That number only gives an order of magnitude since the air expands a lot when it gets hot. If your furnace has a cross-sectional area of, e.g., **0.1 m²**, an air space velocity of **1 m/s** simply indicates that you are running **0.1 m³** of air through it per second.

You have two problems here. First you may need to "blow" if you want a lot of air to move through your furnace. Blowing means that there must be a pressure difference between the air entrance and exit "ports". Second, you must do this blowing against the **air flow resistance** of your air blow apparatus and furnace. The higher that resistance, the higher the pressure you need for blowing the required amount of air through your furnace

To give an example: if you *decrease* the size of you charcoal pieces in order to increase the surface area of the fuel, you also *increase* the air flow resistance through your charcoal bed. That is easy to see. Fill some corn ("maize kernels") into your trumpet and you can still blow though it, albeit with more effort. Fill some corn starch into it and it is "stuffed up". Increasing the pressure will not produce an air flow but at some point you will just blast the obstruction clear out of your trumpet. Make your charcoal pieces too small, and you are in trouble.

● **4. Economy of Size**

There is a considerable economy of size. Large furnaces need less space velocity in order to maintain a certain temperature for a number of reasons, including volume to surface ratio but also because of the "**wall effect**", the observation that the air blown in flows with less resistance (and thus without delivering all its oxygen to the fuel) between the charge and the furnace walls. Altogether, large furnaces are better. You reach higher temperatures or can maintain a certain temperature with less fuel. However, the first law of economics obtains. Furnace operators without powerful air blowers just can't produce enough air to run a big furnace. While the *air velocity* you need to maintain a certain temperature goes *down* about linearly with increasing furnace diameter, the total amount of air needed is airflow *times* cross section, and the cross section increases with the *square* of the furnace diameter. So the air volume you have to blow in still goes *up* at least linearly with the diameter.

Now we can see the basic problem our forebears faced with regard to furnaces throughout the millennia: After you have found suitable materials for building your furnace (able to take the heat and with a low heat conductivity), and a good geometry (round and with cupola domes in the case of kilns to minimize the volume / surface ratio), you are stuck with the **air supply**. Throughout antiquity the methods at your command were not very powerful and that limits the size of your furnace. You had to keep your furnace small - even so it is less efficient.

Note that increasing the space velocity by blowing harder also has limits, especially in small furnaces. If you blow too hard, you will at some point simply blow out the charge through the top of your furnace.
Finally it must be noted that you only can get some air to flow through your furnace if there are interstices between the fuel pieces and whatever constitutes the charge, keeping the air flow resistance from becoming too large. You have that automatically if you crush your charcoal and ore, obtaining irregular pieces with some average size. And that average size matters a lot, as pointed out above. Too large - not enough surface area for generating high heat power. Too small - air flow resistance gets too large and heat power generation goes down. The average size of you charcoal (and ore pieces) should neither be too large nor too small but just right, and that "just right" value scales in some specific way with the size of your furnace and the pressure you can supply for blowing air in.

Direct Bio-Fuels: Facts and Usage

Direct bio-fuels are burnables that haven't been processed by fire or excessive aging. Dried wood, straw, nutshells, or dried dung are direct bio-fuels, charcoals (processed) or coal and oil (long-term aging) are not.

Energy Content of Bio-Fuel
Freshly cut wood is not great for making a fire; in fact this is pretty much impossible for most kinds of wood. It contains too much water - up to 60 % - and needs to be dried first. It still contains some water after drying, and so does presumably dry stuff like chaff or straw. It is difficult to arrive at a water content of less than 10 % for most air dried bio-fuels.

Everybody knows that (dried) hard wood is better for your stove than soft wood since it gives more "warmth", and far better than "straw" that only results in a "straw-fire", quickly burning itself out. That is actually only true of you look at the energy content per *volume*. If you consider energy content per *mass* , all (dry) bio-fuels are about equal and give you around **20 MJ/kg** when you burn them.
In other words: From the energy content alone it doesn't matter much what kind of bio-fuel you shove into you furnace as long as it is the same quantity *by weight*. However, humans throughout the millennia tended to do it *by volume* since is much easier. "Slave, put another basket of wood into the fire" is just easier than "slave, put another kilogram of wood into the fire", since the latter requires that you have a balance and know how to operate it. Energy content, however, isn't the only important criteria for selecting a fuel.

Excess air
Bio fuels heaped up for ignition typically have a lot of free space between the solid material. That makes for a small air flow resistance and thus for easy air passage - but also for a sizeable amount of air streaming through that does *not* participate in the oxidation process. That has several effects:

- The pressure needed for obtaining a certain air space velocity is low. That is good if you only have your (slaves) lungs for blowing.
- A part of the air blown in, called "*excess air*", is not increasing the energy or heat production, which is the only reason why you blow air in. The excess air connected with bio-fuels is seldom less than 25 % of the total and typically around 50 % or more. This is not so good.
- With substantial excess air around, still containing all its oxygen, your furnace atmosphere is *oxidizing* everywhere. Great if that is what you want, not so great if you want to smelt metals, where you need a *reducing* atmosphere.
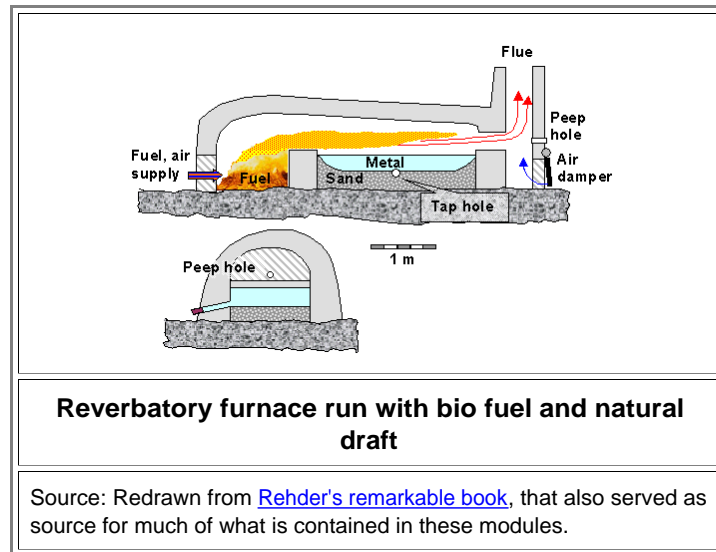
Both water content and excess air decrease the achievable temperature. As a rule of thumb, a 1 % increase / decrease of the water content / excess air, decreases the maximum temperatures by 10 °C, respectively. So even under best conditions with only 10 % water content and 25 % excess air, you loose about 250 °C right away.

Flame Development
On top of your burning woodpile there is lusty colorful flame, whereas you hardly see a flame on top of your charcoal fire. The flame is actually only visible because it contains microscopic hot carbon dust particles that emit light like your hot wire in a light bulb. These dust particles cool off eventually and are nothing but the carbon black (sometimes called soot) you get whenever you see a flame. Moreover the flame is also fed by burning volatile matter that is driven out of the hot bio-fuel. All bio fuels contain a lot of burnable gases or volatile matter; read up about what is called "pyrolysis" here.

A high content of volatiles plus a strong air draft (because of loose piling, for example), gives a long flame. This is a serious waste of energy if the flame comes out of the flue but a possible requirement if you want to heat a **reverberatory furnace** or just a kiln where the heat needs to be transported from the **fire box** to places some way down or up the contraption.

Here is a schematic view of a reverberatory furnace as it was used around, let's say, 1600 (in China) and later (in England) for metal and glass processing. It is about the best you can do.

A long flame is advantageous in this case - you want to heat stuff some distance away from the fire box - so don't use charcoal as fuel. Temperature control was done by controlling the air supply (and the fuel supply, of course) . This could be and was done by adjusting the opening at the fire box side. This, however, interferes with charging new fuel. A more elegant way was to control the air flow at the flue side as indicated. Open an "air short-circuit" hole there, and cold air is sucked in and right out again, reducing the air flow from the fire box.

Air is sucked through by the chimney action or smoke-stack effect and you don't need active blowing.

Reverbatory furnace run with bio fuel and natural draft

Source: Redrawn from Rehder's remarkable book, that also served as source for much of what is contained in these modules.

In a well-designed reverberatory furnace of this kind temperatures of 1400 °C (2552 ° F) could be obtained in the 19th century for charges of several 100 kg, using only a wood fire and natural draft. The problems with the materials used were considerable, and constructions like this would not have been possible in antiquity.

Since the atmosphere is oxidizing, some unwanted impurities contained in your molten metal might oxidize and remove themselves or get included in some slag you provide by adding a flux. That is particularly successful for cast iron with some 4 % carbon. The carbon gets oxidized to CO_2 and disappears. With luck, what is left will be steel. This is known as (one out of many) "**fining" process** for making steel; it was used by the Chinese already 2000 years ago (but in far more primitive contraptions).

Fuel Economy

If you burn a lot of fuel for heating only a small kiln volume or for smelting only a small amount of ore, it will get hotter inside your kiln or furnace compared to using not so much fuel. That is obvious without much science. The ratio of ore to charcoal thus has a major impact on processing temperatures.

A large fuel to ore ratio makes your operation more expensive. Fuel is not for free, especially after you have already cut down much of your forests in the environment of your plant. The ratio of charcoal to ore you supply your smelter with thus goes directly into the costs of what you are making. Of course, with too little fuel you get nothing but with too much you might just waste fuel energy since you don't need the high temperatures produced. Being too hot might even be harmful. Once more you need to be just right.

A lot of pottery throughout the ages was fired around 900 °C (1652 °F), even so firing at higher temperatures makes somewhat better pots, and the potteries definitely were able to produce higher temperatures. It is likely that those old potters simply optimized the cost / performance ratio.

I have stated several times that the old smiths' couldn't get the temperature up enough to melt iron or steel. That is true enough in general but now we must consider that sometimes they may not have wanted to go to the limits of what they could have done. As a case in point, early Western metallurgists in Roman times and later would have had no problem in producing cast iron like the Chinese. They did not do this because they did not want to make cast iron.

Reducing Atmosphere

Wood-fired natural-air draft furnaces and kilns like the one shown here will pretty much always have an *oxidizing* atmosphere as pointed out above. That tends to make your pots reddish because any iron contained in the clay oxidizes to bright red/orange hematite (Fe_2O_3). It also might make your molten metal purer as outlined above. If you can live with that, everything is fine. However, if you like to smelt metal ore or if you want to have your pots black, you need a *reducing* atmosphere, i.e. some carbon monoxide in there. Then you can keep your iron from fully oxidizing, producing black wüstite (FeO) or magnetite (Fe_3O_4) instead of red hematite. And you can smelt your ore.

Using charcoal with an optimized air supply does produce a reducing atmosphere right above the fuel bed. It cannot be the solution for a kiln or reverberatory furnace, however, where you need reducing conditions far away from the fire. What you do in this case is to reduce the air flow by closing the vents to some extent. Adding a quantity of freshly cut green wood might also work. You simply deny the already hot fuel enough oxygen for full burning, encouraging CO production. But all these measures also decrease the temperature and you must take care not to endanger your products.

With cunning you can make black pots this way. With extreme cunning you can make [black or red pots with red or black pictures](#) on it.

But there is just no good way to use furnaces fired by bio-fuels for smelting metals directly. For this we need to go into charcoal technology.