Hot Lime Chemistry 101

Purpose

The purpose of the Hot Lime unit is to provide clean CO_2 into glasshouses to support plant growth. This cannot be achieved through the combustion of biomass alone, due to the presence of various pollutants. Problematic for plants are Ethylene (C_4H_6)m NO_X (Nitrous Oxides), SO_X (Sulphur Oxides) and other combustion residues such as CO, smoke/tars etc...

The delivery of a clean CO_2 by the Hot Lime unit is achieved through two main stages; firstly a charge stage where solid biomass fuel is gasified (or partially combusted) into a combustible gas. This combustible gas is sent into the Hot Lime unit where the CO_2 is captured in the bed. The second stage is a discharge stage, where air is blown into the reactor, thereby releasing a clean CO_2 and air stream. The Hot Lime unit itself is a fixed bed reactor filled with small pellets of Hot Lime material containing iron and limestone to enable these functions.
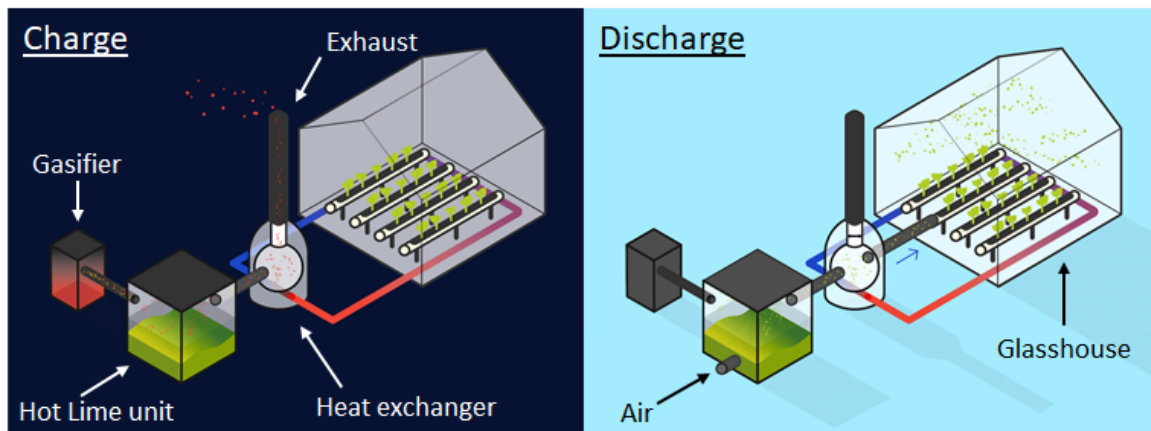

Diagram of the Hot Lime system in (left) charge, where the gasifier feeds the hot lime unit with combustible gases. CO_2 is captured in the Hot Lime unit while pollutants (NO_x, SO_x) are sent out the exhaust stack. In discharge (right) gasification is stopped and air is blown through the system to release the captured CO_2 which is now free of pollutants and is sent to the glasshouse

Gasification

Gasification is a form of combustion, where fuel is burnt with limited oxygen. In conventional combustion, significant effort is placed on ensuring complete combustion, where the only outputs are CO_2 and H_2O. Complete combustion can be difficult to achieve and often incomplete combustion occurs, where some soot or other pollutants are formed such as CO. Gasification is the extreme form of this, where the combustion is starved of oxygen to create a gas that contains a high proportion of combustible material.

For the Hot Lime system, waste biomass from the forestry is fed into the gasifier as wood chips. This biomass is gasified at temperatures of 200-500°C, to form a gas that is approximately; 28% CO, 7% CO_2, 6% H_2, 3% other combustibles and the remainder N_2. Some tars and other long chain hydrocarbons are also formed but these get burnt within the system. Although the purpose of this system is to capture CO_2 and provide this to the glasshouse, it is advantageous to produce a gas composition that is high in combustibles rather than CO_2. This is because the combustible gas is used to store chemical potential energy within the bed (described in more detail below) and through this process is converted into CO_2.

Charge

In the charge phase, the Hot Lime unit receives a mixture of combustible gases, nitrogen and CO_2 from the gasifier. The incoming combustible gases are oxidised by the iron within the bed, thereby reducing the iron species and storing chemical potential energy. The CO_2 generated from the gasifier and the oxidation of the combustible gases is absorbed by the limestone in the bed via a carbonation reaction. These two reactions occur concurrently throughout the bed and are illustrated in the diagram below.
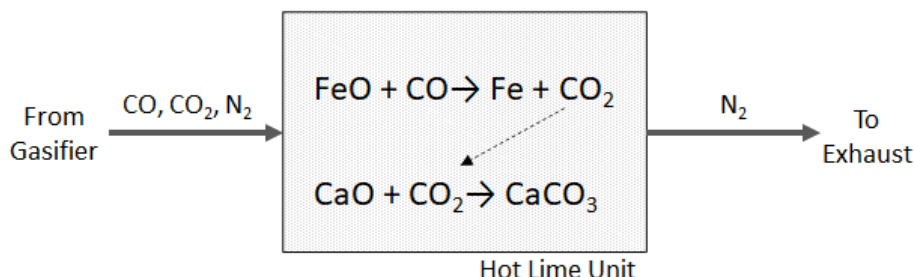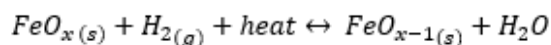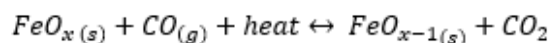

During charge combustible gases from the gasifier are oxidised to CO_2 by the reduction of iron oxide (FeO) to iron (Fe). The CO_2 generated from the gasifier and FeO reduction is captured by carbonation reaction of limestone (CaO) to calcium carbonate ($CaCO_3$)

The reduction of the iron species (oxidation of the combustible gases to CO_2) and carbonation of the limestone to store CO_2 by the limestone are coupled processes. As the oxidation of iron is endothermic and the carbonation of limestone is exothermic, these reactions achieve a thermodynamic equilibrium with each other based on the composition of limestone and iron within the bed. The chemical equations for the oxidation of the iron species and carbonation of the limestone material are shown below.

Carbonation of limestone:

$$CaO_{(s)} + CO_{2\,(g)} \leftrightarrow CaCO_{3\,(s)} + heat$$
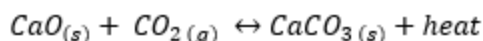
Reduction of iron species (oxidation of combustible gases):

$$FeO_{x\,(s)} + CO_{(g)} + heat \leftrightarrow FeO_{x-1\,(s)} + CO_2$$

$$FeO_{x\,(s)} + H_{2\,(g)} + heat \leftrightarrow FeO_{x-1\,(s)} + H_2O$$

Where x, represents the number of Oxygen atoms bound to the iron. For simplicity, as the reaction proceeds oxygen atoms are stripped from the iron species i.e FeO to Fe or from Fe_2O_3 to Fe_3O_4, or more specifically the oxidation number of the iron atom is being decreased.

As the carbonation reaction proceeds and $CaCO_3$ (Calcium carbonate) is formed, CO_2 is removed from the system. The lower CO_2 concentration drives the equilibrium of the Fe reduction equations to the right, to produce more CO_2, which then drives the formation of more CO_2 and then $CaCO_3$. This process continues until the thermodynamic limit of CO_2 storage in the $CaCO_3$ is achieved, which is a function of the bed temperature due to the equilibrium partial pressure of CO_2 above CaO.

The equilibrium partial pressure of CO_2 is shown in the table below. As the temperature increases, the equilibrium partial pressure of CO_2 reduces, meaning that the CO_2 will favour existing in as CO_2 gas above the solid CaO rather than as $CaCO_3$. Therefore, the system is designed to operate within the 600-750°C where the CO_2 will favour existing as $CaCO_3$ to maximise the amount of CO_2 stored. It is important to note that the system is governed by these thermodynamic limitations rather than any kinetic limitations of these processes.
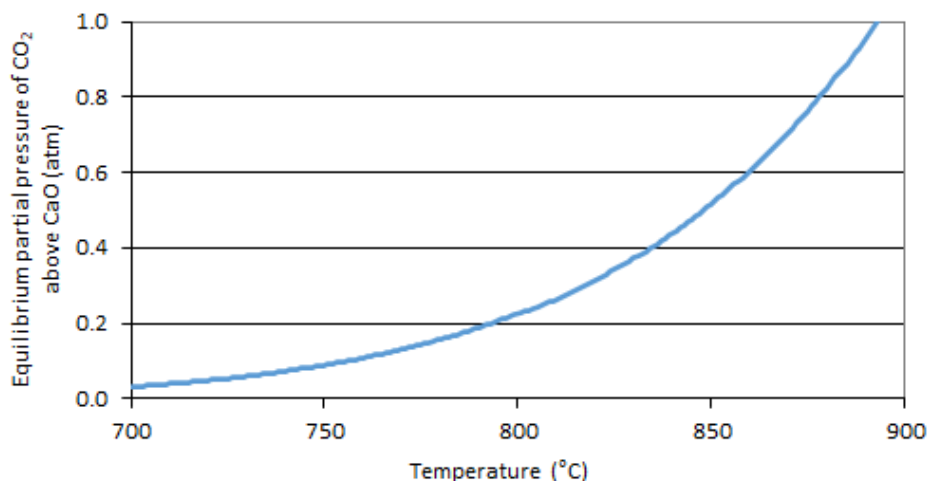

Equilibrium partial pressure of CO₂ above CaO

Overall, this charge process enables the conversion of solid biomass fuel into CO_2 and heat, which is stored within the Hot Lime unit. Excess heat produced during this period, not captured in the bed, is recovered using heat exchangers to provide heat into the glasshouses.

Discharge

The discharge stage denotes the release of the CO_2 stored within the bed as $CaCO_3$ during the charge stage. The release of CO_2 is performed by blowing air into the Hot Lime unit. As air contacts the reduced iron species, a highly exothermic oxidation reaction proceeds quickly and generates large amounts of thermal energy. The release of this stored chemical potential energy heats up the bed. Previously in charge, the amount of CO_2 captured was based on the bed temperature, as this determined the equilibrium partial pressure of CO_2 above the CaO. The same concept is used here, as the bed temperature increases due to the oxidation of the iron species, the equilibrium partial pressure of CO_2 increases and therefore CO_2 is released. Equations governing this discharge and diagram of this process are detailed below.
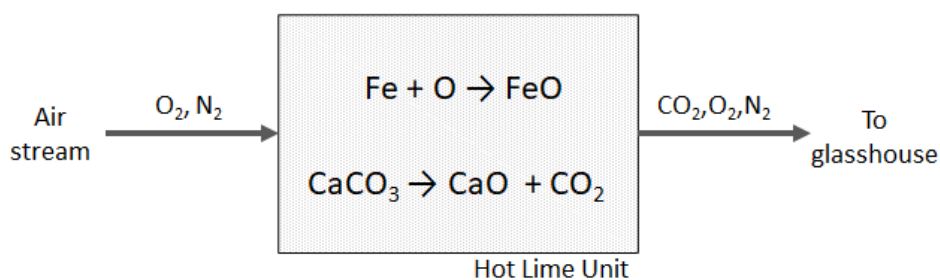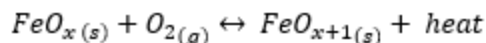

Oxidation of iron species from iron (Fe) to iron oxide (FeO), releasing energy to enable the calcination of calcium carbonate ($CaCO_3$) to limestone (CaO) to release carbon dioxide (CO_2) during discharge.

Calcination of calcium carbonate:

$$CaCO_{3\,(s)} + heat \leftrightarrow CaO_{(s)} + CO_{2\,(g)}$$

Oxidation of iron species:

$$FeO_{x\,(s)} + O_{2\,(g)} \leftrightarrow FeO_{x+1\,(s)} + heat$$
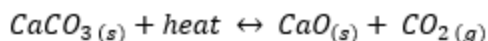
Similar to in charge, the reactions within the bed are coupled. The oxidation of the iron provides sensible heat to raise the bed temperature but also provides heat for the endothermic calcination of $CaCO_3$ back to CaO. The coupling of these equations makes the process inherently self-regulating as the vast amount of heat generated is converted into chemical potential energy by forming CaO and is therefore a safe, controllable and predictable process.

Overall, this discharge process releases the CO_2, stored within the bed and returns the bed to its initial state. The gasifier is not operated discharge, as the purpose of the gasifier is to charge the bed with CO_2. Separating these charge and discharge states removes the possibility of NO_X, SO_X and other combustion pollutants being present, enabling a clean CO_2 stream to be supplied to the glasshouse.