Thesis summary :

"Study of the microstructural transformations of clay/biomass mixtures during firing and relationships with mechanical and thermal properties".

Project objective :

Controlling the water supply rate of a plant structure by using a microporous clay pellet.

Relevance of the thesis :

Clay after firing is by nature one of the known microporous structures. The aim of this thesis is to study and control the porosity of clay bodies during a clay/biomass mixture as well as the evolution of the mechanical properties related to this mixture.

Clay composition and structural impact during firing in the absence of biomass :

Clays are mainly divided into three categories:

- Earthenware clays (biscuit firing between 900 and 1100 degrees)
- Sandstone clays (fired between 1100 and 1280 degrees)
- Ceramic clays (fired between 1100 and 1280 degrees)

The project focuses on earthenware clays, the most favourable clay for the creation of porous structures.

A clay object usually undergoes **two firing stages**:

- First of all, **the biscuit**, which consists of a first firing of the clay with a slow rise in temperature and composed of firing stages. The aim of this firing is the complete dehydration of the structure (occurs around 400 degrees) and then its dehydroxylation (removal of all hydrogen bonds in the structure) which occurs around 600 degrees. This evaporation and the accompanying structural rearrangement is the source of the porosity of the clay structures.
- **Glazing,** which consists of depositing and firing a vitreous layer on the biscuit. This process is at the heart of the sealing phenomenon of clay-based objects. For obvious reasons we will not concentrate on this process.

Porosity factor (without biomass) :

The percentage of degreaser: Indeed, a block of clay sold in the market is not composed of 100% clay but mixed with a "degreaser". In the framework of the thesis, the composition was 70% clay body for 30% degreaser. The role of the degreaser is to promote the removal of water and gases from the structure. This release of fluid is the key to the creation of porosity in the structure and is logically accompanied by an increase in volume but a decrease in density of the material.

Percentage of quartz in the structure: Above 573°C, quartz undergoes molecular rearrangement responsible for an overall structural expansion of 0.3% in the clay used.

Temperature rise: Clay is a water-laden material. Its firing is therefore accompanied by an important evaporation phenomenon responsible for most of the porosity of clay bodies (the evaporation of hygroscopic and interposition water is compensated for by the entry of air within the material). The faster the firing temperature rises (mainly in the first 200 degrees), the more brutal the gas release and therefore the greater the porosity of the clay. A slow rise in temperature gives the still malleable clay time to rearrange its structure (collapse under its weight) and therefore minimises the porosity phenomenon. The counterpart of this high porosity during a rapid temperature rise is the weakening of the structure which can lead to the creation of micro-fractures or even cracks of constitution visible to the naked eye.

Maximum temperature reached (sintering principle): Sintering is a phenomenon specific to granular materials (powder for example) and which consists of the rise in temperature without reaching the melting point of the materials in order to create inter-particle bridges. These bridges are at the origin of the structural reinforcement of the clay during its firing. This process becomes particularly significant from 850 degrees and has as a direct consequence the reduction of the porosity of the material, the bonds created coming to obstruct the pores present (This explains why earthenware has a higher porosity rate than stoneware or ceramics). Around 700 degrees, on the other hand, the first consequence of sintering is the release of carbon dioxide, which is responsible for an increase in the wide porosity of the material.

Clay composition and structural impact during firing in the presence of biomass :

Initial conditions :

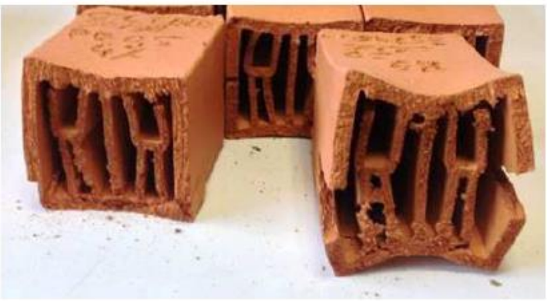
The plant materials were incorporated into the products discussed in the previous chapter during the production of the clay mixes and then followed the same process. The agricultural residues were first added to the clay soil and the degreaser at 4% by mass and dispersed with a mixer by adjusting the water content to 17%. The clay pastes were then rolled to 0.8mm to be extruded into solid platelets with dimensions of 180x80x18mm3 and thin-walled briquettes with a view to the industrialization of the mixtures. The products were then dried at temperatures of up to 105°C in a progressive manner and fired at the same usual temperature, equivalent to 940°C.

Determination of the equilibrium point of the mixture of biomass, degreaser, clay bodies:

A structural problem arose following these initial tests. The plasticity of the clay bodies, initially due to the clay-degreasing equilibrium, was weakened by the presence of biomass, which has a much lower plasticity.

Test result :

Figure 4.1 – Briquettes extrudées et cuites en dépit d'un défaut de plasticité.



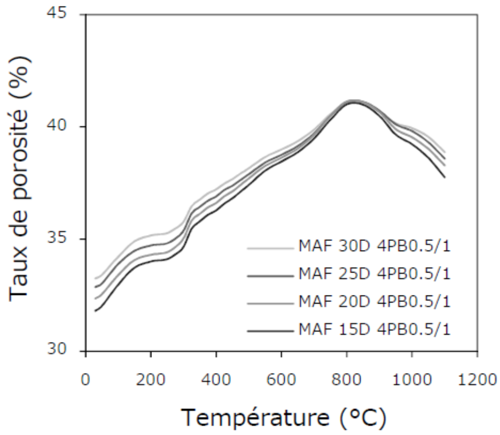
The solution found was the rebalancing between biomass and degreaser by iterative processes as follows:

Tableau 4.1 – Etablissement et répartition des formules de mélange argileux de fabrication *(MAF)* avec le dégraissant *(D)* et la matière végétale *(MV)*.

Teneur en matière végétale (%)	Teneur en dégraissant (%)	Formule
0	30	MAF 30D 0MV
2	25	MAF 25D 2MV
4	20	MAF 20D 4MV
6	15	MAF 15D 6MV
8	10	MAF 10D 8MV

The ideal plasticity balance that emerges is a composition of 4% biomass, 20% degreaser and 76% clay bodies.

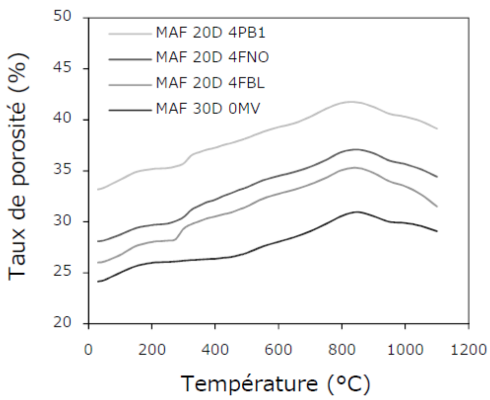
A subsequent study of the porosity rate tends to show that the decrease in degreaser content also decreases the porosity rate significantly after 850 degrees, important information to take into account when finding the right porosity/plasticity balance.



Stiffness/Porosity balance as a function of the biomass used :

Following several tests using different biomass sources (olive stone flour, wheat flour, wheat straw). An important initial variation in the porosity of the mixture was observed due to the high water content of the biomasses used, a porosity that is maintained during the firing process. An initial conclusion therefore tends to show an increase in the porosity rate with the counterpart of a more complex structural equilibrium to be reached when incorporating biomass up to 4%.
At the previously found equilibrium mixing point (4% biomass, 20% degreaser, 76% clay body) an experimental analysis shows a Young's modulus significantly close to a classical clay without biomass. This phenomenon is linked to the transformation of the biomass into carbon chains during its calcination. Flour, being denser and having a small particle size (compared to straw), favours the creation of particle bridges but therefore has a lower porosity than wheat straw. Wheat straw therefore seems to be an interesting material to study in the framework of the project.

Figure 4.6 – Evolution du taux de porosité au cours de la cuisson de produits soumis à une incorporation de 4% en masse de PB_1, de FNO et de FBL.



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structure, even to the point of collapse, due to plastic imbalance, which was finally corrected by reducing the percentage of degreaser in the mixture.
In parallel to this, we observe as a direct consequence of the addition of plant matter, an increase in the porosity of the structure linked to the release of

gases (mainly water vapour). Porosities whose average diameters are strongly correlated with the granulometric diameter of the biomass used. The direct consequence of this increase in porosity is the embrittlement of the structure as explained above, associated with a decrease in the thermal conductivity of the material due to the presence of porosities.
It is recalled that this biomass/degreaser balance becomes impossible for a biomass rate exceeding 8%.
The study carried out in the thesis also shows how the type of biomass impacts the porosity/mechanical strength balance.

Conclusion related to the initial objective of creating a microporous clay structure:

From the reading of this thesis, I can conclude that the parameters I will manipulate for the control of porosities are :

- The maximum temperature reached during cooking
- The speed of heating during cooking
- The ratio of biomass to incorporated degreaser
- The type of biomass incorporated and its particle size

An ideal setting to be tested for maximum porosity without endangering the structure seems to be in the reading of this thesis:

- A maximum temperature between 850 and 900 degrees
- A heating rate of 100 degrees for the first hour followed by a heating rate of 150 degrees per hour until 600 degrees is reached. Then finish the cooking by increasing the temperature by 200-250 degrees per hour until 850/900 degrees is reached.
- A biomass/degreaser ratio of 4%/20% respectively to ensure sufficient structural balance
- The use of wheat straw pellets.