2nd International Conference on Bio-based Building Materials &
1st Conference on ECOlogical valorisation of GRAnular and FIbrous materials

ICBBM EcoGRAFI

June 21th - 23th 2017
Clermont-Ferrand, France

CHEMICAL AND HYGROTHERMAL CHARACTERIZATION OF AGRO-RESOURCES' BY-PRODUCT AS A POSSIBLE RAW BUILDING MATERIAL

M. Viel*, F. Collet, C. Lanos

Université Rennes 1, Laboratoire Génie Civil et Génie Mécanique, BP 90422, Rennes, France

* Corresponding author: marie.viel@univ-rennes1.fr

Abstract

The ISOBIO project proposes an innovative strategy to bring bio-based construction materials into the mainstream. A key innovation consists of the use of bio-based aggregates from a local culture, with green binders for the production of ecofriendly composites. This work aims to combine existing technologies in order to develop bio-based panels with high insulating properties, low embodied energy, low embodied carbon and hydrothermally efficient. This study aims to value the agro-resources by-products from flax, hemp, corn, rape and wheat, provided by one of the project partner, for find out new alternative materials that respond to sustainable development criteria. In the present work, the chemical characterization of agro-resources's by-product are studied by Van soest method and Phenol sulfuric method to determine the content of cellulose, hemicellulose, lignin and polysaccharides. Measurement of thermal conductivity and Moisture Buffer Value are also achieved in these raw materials to determine their hygrothermal properties at bulk density. Thermal Conductivity and MBV evolve according to the density whatever the agro- resources type. All these materials have different properties but they are all excellent hygric regulators. These results suggest that agro-resources's by-product may be used as a raw building material but not for the same types of use. In fact, some raw materials would be more suitable for thermal insulating products and others would be better suited to indoor facing panels.

Keywords:

Sustainable building materials, Hemp shiv, Flax shiv, Rape straw, Wheat straw, Corn cob, Van soest method, Phenol sulfuric method, Moisture Buffer Value, Thermal conductivity

1 INTRODUCTION

In recent years, the quantity of agricultural waste has been rising rapidly all over the world and will continue to increase rapidly. More, several studies, which estimate the availability of crop residues in 2020 or 2030 in Europe, have been produced. Thus, all these studies show that the availability of crop residues will continue to increases more and more quickly [Searle 2013].

As a result, the environmental problems and negative impacts of agricultural waste draw more and more attention. Therefore, there is a need to adopt proper approaches to reduce and reuse agricultural waste. The agricultural residues mainly consist of different straws, such as wheat or maize. A wide range of agricultural waste could potentially be used to produce biomaterials, aiming at the valorization of the whole biomass and basing on a zero-waste concept, such as biofuels, food and feed ingredients, chemicals and buildings materials [Fava 2015; Hameed 2014].

Recently, the Isobio project was initiated. This project, supported by the European Union Horizon 2020 program, proposes an innovative strategy to bring bio-based construction materials into the mainstream. A key innovation consists in using bio-based aggregates from a local culture with green binders to produce ecofriendly composites. This work aims to combine existing technologies in order to develop bio-based panels with low embodied energy, low embodied carbon and high hygrothermal efficiency.

This study aims to value five agro-resources' by-products from flax, hemp, corn, rape and wheat, produced in France, to find out new alternative materials that meet the sustainable development criteria. In this work, the chemical and physical properties of these agricultural by-products, are measured and compared. Composition is studied by Van soest method and Phenol sulfuric method to determine the content of cellulose, hemicellulose, lignin and pectin. Thermal conductivity and moisture buffer value are investigated. Finally, the conclusions are drawn and the potential uses of the agro-resources' by-product in building materials are highlighted.

2 MATERIALS AND METHODS

2.1 Materials

This study is performed on five kinds of raw materials with different particle size distributions, collected and processed by CAVAC Company (Vendée, France) in 2015. The bio-based aggregates are obtained through an industrial defibering process by mechanical breaking. In fact, to separate the shiv from the fibre, straw bales are opened, crushed with a hammer mill and sorted into three different categories: fines, fibres and shiv, during the separation process. Only hemp and flax can be changed in fines and fibres. The fines are vacuumed in several process steps. Finally, the shiv are calibrated with different sieving grids (n°7, n°8, n°12 and n°14) using a grader. The uncalibrated shiv go back to hammer mill step (Fig. 93).

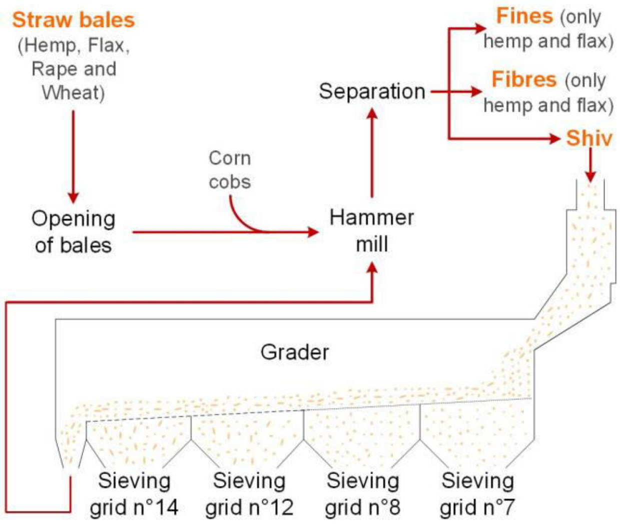

Fig. 93: Bio-based aggregates processing flow-chart

The 17 selected bio-aggregates are the following (G=grid diameter used to grade the aggregates, *Fig. **94***):

- Hemp shiv (*Cannabis sativa L., Futura 75*): G7, G8, G14 and fines
- Flax shiv (*Linum Usitatissimum L., Angora*): G7, G8, G12, G14 and fines
- Rape straw: G7, G8 and G14
- Wheat straw: G7, G8, G12 and G14
- Corn cobs

The species and variety of rape, wheat and corn are unknown because they are cultivated for their seeds. Therefore, straws or cobs, which are by-products, are mixed without distinctions between variety or species before being sold by the trading. These raw materials are grown in Vendée (France).

Different physical characterization were performed in laboratories as bulk density or particle size distribution. *Tab.* ***47*** and *Tab.* ***48*** summarize the bulk density, the particle size mass fraction distribution, the dust content and the fiber content.

Bulk density was measured at dry state following the recommendations of the Rilem TC BBM [Amziane 2017]. The bulk density of all tested aggregates ranging from 29 to 373 kg/m^3 logically decreases when the size of aggregate increases.

The particle size distributions lead to the evaluation of complementary particle geometrical parameters: width and length of particles, elongation, dust content and fibre content. Size distribution was determined by image analysis of scanned samples (based on the recommendations of the Rilem TC BBM, [Amziane 2017]) or by laser granulometry (using the Malvern Mastersizer 2000 apparatus with the Scirocco 2000 dry dispersion unit). Globally, the particle size (width and length) increases with the grader grid number. The dust content ranges from 0 % for corn cob to 1.17% for G7 wheat straw. Only hemp and flax include fibres. Conversely to dust content, the biggest the shiv is, the highest the fibre content is (except for G14 hemp shiv).

Tab. 47 : Bulk density at dry state and PSD (mass fraction) of fines (hemp and flax)

Raw materials		Hemp fines	Flax fines
Bulk density at dry state (kg/m^3)	Av.	133.21	140.30
	σ	4.24	3.26
	CoV	3.19%	2.32%
r_{10} (laser)		0.100	0.112
r_{50} (laser)		0.502	0.564
r_{90} (laser)		1.262	1.125

2.2 Methods for chemical characterization

Van Soest Method

The Van Soest method consists in successive extractions to determine the composition of a vegetal sample (Fig.

Fig. 94 : Photos of agro-resources' by-product

Tab. 48: Bulk density at dry state and PSD (mass fraction) of hemp shiv, flax shiv, rape straw, wheat straw and corn cob

Raw materials		Hemp shiv			Flax shiv				Rape straw			Wheat straw				Corn Cob
		G7	G8	G14	G7	G8	G12	G14	G7	G8	G14	G7	G8	G12	G14	
Bulk density at dry state (kg/m^3)	Av.	104.01	87.89	96.65	111.28	129.91	93.69	90.72	88.06	78.71	73.20	53.89	49.70	29.69	31.20	372.75
	σ	1.44	0.62	2.70	3.49	3.05	1.48	1.61	1.05	2.13	0.93	0.51	2.35	1.20	1.18	3.66
	CoV	1.38%	0.71%	2.79%	3.14%	2.35%	1.58%	1.77%	1.19%	2.71%	1.28%	0.95%	4.73%	4.04%	3.79%	0.98%
w_{10} (mm)		1.051	1.257	2.353	0.842	0.898	0.939	0.864	1.050	1.278	1.780	0.848	0.866	1.381	1.239	2.249
w_{50} (mm)		2.105	2.319	4.215	1.402	1.480	1.509	1.485	1.967	2.159	3.079	1.700	1.721	2.360	2.169	3.784
w_{90} (mm)		3.761	4.042	6.275	1.987	2.090	2.257	2.275	3.186	3.389	5.550	2.977	3.005	3.921	3.703	4.765
L_{10} (mm)		3.238	3.859	10.361	3.715	3.242	4.878	4.871	3.005	4.593	8.754	4.112	4.127	11.906	9.463	3.374
L_{50} (mm)		6.703	7.615	17.622	7.014	6.282	9.490	9.509	7.073	9.239	15.922	9.331	8.819	22.466	17.931	5.145
L_{90} (mm)		12.360	13.100	29.993	12.763	11.720	16.753	18.495	14.639	16.362	27.270	22.031	19.106	39.022	30.901	6.472
ε_{10}		1.765	1.849	2.481	2.615	2.291	3.115	3.301	1.509	1.995	2.630	2.488	3.080	4.856	3.872	1.142
ε_{50}		3.052	3.142	4.250	5.204	4.349	6.262	6.582	3.585	4.345	5.105	6.013	6.544	9.482	8.372	1.357
ε_{90}		5.678	5.655	7.921	10.154	8.418	12.270	12.793	7.714	8.936	9.789	12.861	12.920	17.845	15.535	1.756
Dust content		0.80%	0.65%	0.04%	0.46%	0.74%	0.25%	0.21%	0.31%	0.14%	0.02%	1.17%	1.03%	0.05%	0.06%	0.00%
Fibre content		5.01%	6.51%	2.31%	4.64%	1.66%	5.37%	8.09%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

95**).**

The raw materials are crushed and sieved through a 1mm mesh. Then, 800 mg of sample are collected and introduced in porous bag. The first extraction is realized with NDF (Neutral Detergent Fiber) solution, in the ANKOM 2000 Automated Fiber Analyzer at 100°C during 1 hour, to remove soluble cell contents like fat, wax, pectin, proteins and polysaccharides. The remaining fraction contains cellulose, hemicellulose, lignin, and minerals. ADF (Acid Detergent Fiber) solution is used for the second extraction which lasts 1 hour at 100°C, to remove hemicellulose. The remaining fraction contains cellulose, lignin, and minerals. The last extraction is realized with ADL (Acid Detergent Lignin) solution which is 72% sulfuric acid, in Daisy incubator (Ankom) during 4 hours. During this last extraction, cellulose is hed off leaving only lignin and recalcitrant materials. After each extraction, porous bags are rinsed in water, is hed with acetone and dried overnight at 103°C. Then, the calcination of the samples at 550°C for 3 hours is done to determine the ash content [Contreras 1999; Carrier 2011; Van Soest 1991].

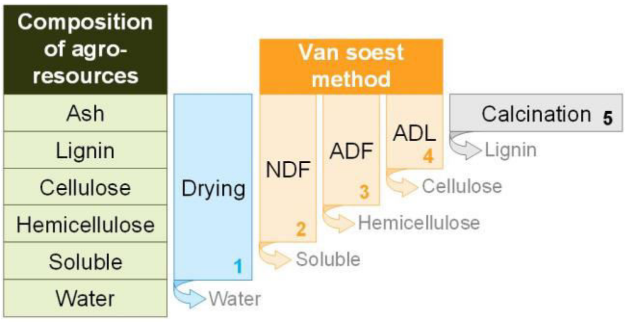

Fig. 95: Synthetic sketch of Van Soest Method allowing accessing the biomass composition [Carrier 2011]

The soluble, cellulose, hemicellulose, lignin and minerals contents of each sample are estimated with the equations (1) to (5).

$$\%_{Ash} = \frac{W_{550} - W_{crucible}}{W_{sample} \times \%_{DM}} \quad (1)$$

$$\%_{Lignin} = \%_{ADL} = \frac{W_{ADL} - (W_{bag} \times CC_{ADL}) - (W_{550} - W_{crucible})}{W_{sample} \times \%_{DM}} \quad (2)$$

$$\%_{Cellulose} = \%_{ADF} - \%_{ADL} = \frac{W_{ADF} - (W_{bag} \times CC_{ADF}) - (W_{550} - W_{crucible})}{W_{sample} \times \%_{DM}} - \%_{ADL} \quad (3)$$

$$\%_{Hemicellulose} = \%_{NDF} - \%_{ADF} = \frac{W_{NDF} - (W_{bag} \times CC_{NDF}) - (W_{550} - W_{crucible})}{W_{sample} \times \%_{DM}} - \%_{ADF} \quad (4)$$

$$\%_{Soluble} = \frac{(W_{sample} \times \%_{DM}) + (W_{bag} \times CC_{NDF}) - (W_{550} - W_{crucible})}{W_{sample} \times \%_{DM}} \quad (5)$$

with:

- **W_{sample}:** weight of the sample
- **$\%_{DM}$:** percentage of dry matter
- **W_{NDF}, W_{ADF} and W_{ADL}:** weight of the sample with the porous bag after the first, second or last extraction
- **W_{550}:** weight of the sample after the calcination with the crucible
- **W_{bag}:** weight of the porous bag
- **$W_{crucible}$:** weight of the crucible
- **CC_{NDF}, CC_{ADF} and CC_{ADL}:** correction coefficient for the porous bag after the first, second or last extraction

Phenol Sulfuric Method

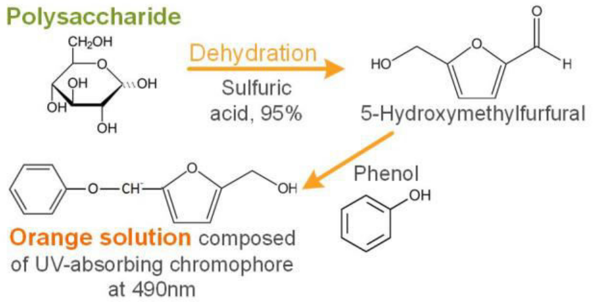

Fig. 96: Schematic overview of the phenol sulfuric method for the total carbohydrate analysis

The phenol sulfuric method consists in total carbohydrate content dosage. Like for the Van Soest method, the raw materials are crushed and sieved through a 1mm square mesh. Then, 3.0 mg of sample are collected and introduced in test tube. After, 9 ml distilled water, 3 ml 5% solution (%w/v) of phenol/water and 15 ml concentrated sulfuric acid are added. Test tube is mixed thoroughly and leave for 30 minutes minimum. The sulfuric acid causes the hydrolysis of the osidic links and the dehydration of the released monosaccharides to form furfural derivatives which react with the phenol and give the orange color to the solution (Fig. 96). The absorbance of the sample solution is measured by a UV-Visible spectrophotometer in the range 550 to 400 nm. The maximum absorbance read off the sugar content in mg/l from the calibration curve which is established for the range of D(+)xylose (5 - 67 mg/l) [Dubois 1956; Evon 2008]. The amount of color is proportional to the amount of furfural, so the percentage of D(+)xylose is converted to furfural by using a coefficient of 92.5% [Dubois 1956].

2.3 Methods for physical characterization

Thermal conductivity

The thermal conductivity is measured on bulk aggregate, at 23°C and dry state, following the recommendation of the Rilem TC BBM [Amziane 2017]. The device consists in two containers filled with bulk aggregates. The sensor is embedded between the two containers (Fig. 97). The sensor used is a five centimeter long hot wire. The heat flow and heating time are chosen to reach high enough temperature rise (>10°C) and high correlation coefficient (R^2) between

experimental data and fitting curve given equation **Error! Reference source not found.**7). The heating power is 0.142 W and the heating time is 90 s.

$$\Delta T = \frac{q}{4\pi\lambda}(ln(t) + K) \qquad (8)$$

where q is the heat flow per meter (W.m^{-1}) and K is a constant including the thermal diffusivity of the material. The sensor is regularly checked by measuring thermal conductivity of reference material which thermal conductivity is 0.039 W/(m.K).

The containers allow to control the bulk density of aggregates. Their size is chosen to be height enough to ensure that heat flux stays in the sample. Their diameter is twice the length of the sensor. The container is thus 10 centimeters in diameter and 7.5 cm in height. When the sample is prepared, its bulk density is checked to ensure representativeness of the material. The upper side of the top container is covered with a plate to prevent any moisture exchange during measurement. The measurement of thermal conductivity is repeated 5 times for each material. According to the manufacturer, the hot wire is well adapted for the measurement of thermal conductivities ranging from 0.02 to 5 W.m^{-1}.K^{-1} and the expected accuracy is 5%.

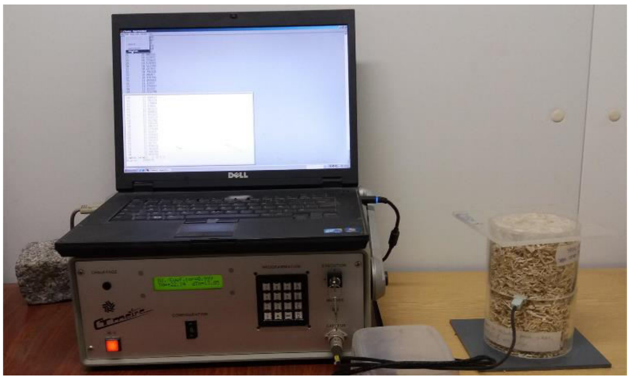

Fig. 97: Experimental device for the measurement of thermal conductivity

Moisture Buffer Value

The moisture buffer value MBV of materials quantifies their ability to moderate the variations of surrounding air. It is measured according to the method defined in the NORDTEST project [Rode 2005]. This value relates the amount of moisture uptake (and release), per open surface area, under daily cyclic variation of relative humidity as shown in the following equation:

$$\boldsymbol{MBV} = \frac{\boldsymbol{\Delta m}}{A \times (\boldsymbol{RH_{high}} - \boldsymbol{RH_{low}})} \qquad \textbf{(9)}$$

Where MBV is the Moisture Buffer Value (g/(m².%RH)), Δm is the moisture uptake / release during the period (g), A is the open surface area (m²) and $RH_{high/low}$ are the high/low relative humidity level (%).

Within the NORDTEST project, a round robin test is performed on nine representative building materials. It gives initial results and leads to a classification of moisture buffer values from negligible to excellent (Fig. 98).

In this study, the samples are put in containers of about 12 cm in diameter. The volume of the samples is about 800 to 1000 cm^3. The average horizontal air velocity is 0.07 m/s, which meets the requirement of the Nordtest Project protocol.

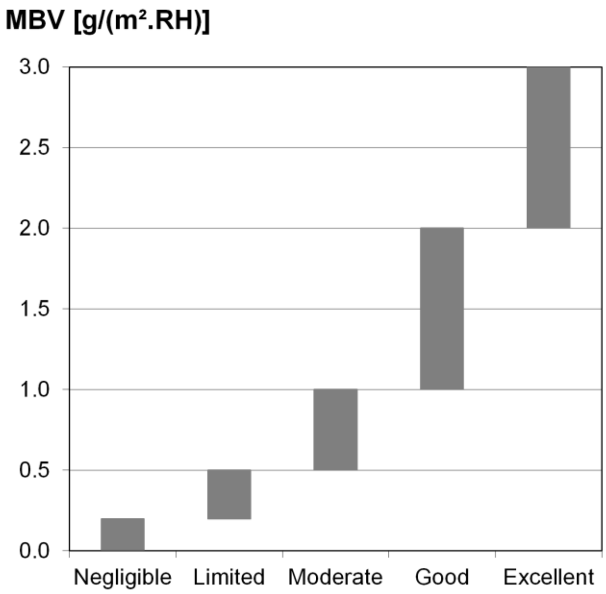

Fig. 98: Nordtest project classification of materials versus Moisture Buffer Value

Tab. 49: Chemical composition of agro-resources by the Van Soest method

Agro-resources	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Soluble (%)	Ash (%)
Hemp shiv	49.97 ± 1.63	21.42 ± 3.32	9.52 ± 1.17	17.75 ± 2.85	0.67 ± 3.32
Flax shiv	44.63 ± 1.44	24.41 ± 2.64	20.98 ± 1.01	7.56 ± 3.36	1.48 ± 0.04
Flax fines	28.51 ± 2.76	15.80 ± 1.65	18.14 ± 1.55	29.15 ± 1.22	4.20 ± 1.56
Rape straw	53.06 ± 1.07	18.13 ± 3.28	9.63 ± 3.33	17.68 ± 4.56	0.79 ± 2.54
Wheat straw	43.04 ± 0.38	29.66 ± 2.90	5.24 ± 0.18	20.43 ± 3.81	0.82 ± 2.04
Corn cob	36.78 ± 2.60	38.81 ± 1.86	3.30 ± 3.02	19.30 ± 5.84	0.46 ± 1.86

Tab. 50: Chemical composition (cellulose, hemicellulose, lignin, soluble and ash) of agro-resources based on the scientific literature

Agro-resources	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Soluble (%)	Ash (%)	Ref.
Hemp shiv (Cannabis sativa L., LCDA - France)	44.00	18.00	28.00	8.00	2.00	[Vignon 1995]
Hemp shiv (Cannabis sativa L., Futura, Italy)	51.60	21.50	12.90	12.90	6.60	[Cappelletto 2001]
Hemp shiv (average on 15 references)	47.50 ± 3.50	6.40 ± 1.50	8.00 ± 1.00	29.40 ± 3.60	8.80 ± 1.00	[Godin 2010]
Flax shiv (Canada)	38.06 ± 0.57	25.03 ± 0.57	31.20 ± 0.22	4.00 ± 0.27	1.71 ± 0.05	[Ross 2010]
Flax shiv (Linum Usitatissimum L.)	53.00	13.00	24.00	1.50	> 2%	[Sain 2002]
Rape straw (Poland)	37.55	31.37	21.30	3.76	6.02	[Greenhalf 2012]
Wheat straw	38.60	32.60	14.10	-	5.90	[Sun 2000]
Corn cob (average on 10 species - Austria)	38.80 ± 2.50	44.40 ± 5.20	11.90 ± 2.30	5.21 ± 1.1	2.88 ± 0.11	[Pointner 2014]

Tab. 51: Content of pectin in agro-resources' by-product

Agro-resources	Pectin (%)	[Pectin] / [Soluble] (%)	Corrected Pectin (%)	[Corrected Pectin] / [Soluble] (%)
Hemp shiv	13.95 ± 0.36	78.59	9.19	51.77
Flax shiv	17.19 ± 0.93	227.44	6.71	93.20
Flax fines	17.48 ± 1.13	59.96	8.41	28.85
Rape straw	19.34 ± 0.83	109.41	14.53	82.15
Wheat straw	20.58 ± 1.46	100.73	17.96	87.92
Corn cob	19.99 ± 0.57	103.60	18.34	95.05

Tab. 52: Content of pectin, protein and lipid in agro-resources based on the scientific literature

Agro-resources	Pectin (%)	Protein (%)	Lipid (%)	Reference
Hemp shiv (Cannabis sativa L., LCDA - France)	4.00	3.00	1.00	[Vignon 1995]
Rape straw (Korea)	19.40 ± 0.50	1.60 ± 0.10	-	[Jeong 2011]
Corn cob (average on 10 species - Austria)	0.67 ± 0.12	4.26 ± 0.96	0.30 ± 0.02	[Pointner 2014]

3 RESULTS AND DISCUSSIONS

3.1 Chemical Characterization

Van Soest Method

The content of cellulose, hemicellulose, lignin, soluble and ash, determined by the Van Soest method, from agro-resources' by-product, are shown in Tab. 49. Soluble is mainly composed of pectin, protein and lipid (fat and wax). Large differences in the chemical composition between these raw materials are evident. On a dry-weight basis, agro-resources' by-product contain 55 - 95% of polysaccharides (cellulose, hemicellulose and pectin). The cellulose is the most abundant component in the plant cell, except in the case of the corn cob. The cellulose is present in all the different walls of plant cell, in the form of cellulose microfibrils (fiber-like strand), randomized in the primary wall and then in parallel of varying inclination according to the layer of the second wall. Cellulose microfibrils has a rigid structure, formed from many cellulose molecules, in order to create the strong support structure that allows agro-resources to stand upright. Between the cellulose microfibrils, hemicellulose forms network and is the second component of plant cells. In the second wall, lignin which is the second most abundant polymeric organic substance in plant cell walls, acts as a cement, has a supportive structural function and also protects the cellulose and hemicellulose agro-resources to stand upright. Between the cellulose microfibrils, hemicellulose forms network and is the second component of plant cells. In the second wall, lignin which is the second most abundant polymeric organic substance in plant cell walls, acts as a cement, has a supportive structural function and also protects the cellulose and hemicellulose [Chen 2014; Sorieul 2016].

Corn cob has the lowest lignin and ash content (3.30% and 0.46%) but the highest hemicellulose content (38.81%). Flax fines have the lowest hemicellulose and cellulose contents (15.80% and 28.51%) but the highest soluble and ash content (29.15% and 4.20%). Flax shiv has the lowest soluble content (7.56%) but the highest lignin content (20.98%). Rape straw has the highest cellulose content (53.06%).

In Tab. 50, these values are compared with these in the scientific literature. The composition are not exactly identical, even when agro-resources are the same variety and specie. Indeed, the chemical composition also depends on the area of production, the weather (sunlight, relative humidity, temperature, rainfall and wind) and the maturity of the plant [Kymäläinen 2008; Vignon 1995]. Agro-resources adapt to the environment in which they grow. Generally speaking, agro-resources from CAVAC (Vendée, France) contain less lignin and ash, and more soluble compared to the composition of lignocellulosic biomass resources in the scientific literature.

Phenol Sulfuric Method

Tab. 51 gives the content of pectin in different agro-resources determined by phenol-sulfuric method. Pectin is complex macromolecule, as it can be composed out of as many as 17 different monosaccharides containing more than 20 different linkages. Pectin is present, in the cell plant, in the middle lamella, primary wall and second walls. Pectin plays several roles in the growth plant period: lends strength and supports to the plant, activates plant defense responses, and induces a lignification [Voragen 2009]. Following Tab. 51, almost all soluble are composed with pectin. For flax shiv, rape straw, wheat straw and corn cob, the quantity of pectin is higher than the quantity of soluble. This is due to pectin extraction process. Indeed, cold water allows to solubilize pectin and part of hemicellulose but no cellulose [Gao 2014; Silva 2014]. Flax shiv is the bio-based aggregates which has the biggest difference between the quantities of pectin and soluble, it's also the agro-resource which has the highest quantity of lignin. More, in Van soest method, the lignin is removed with 72% sulfuric acid at room temperature and the lignin is allowed to form chromophore [Dyer 1999] which interacts with those of phenol sulfuric method. So, the quantity of pectin is corrected by subtracting 50% of lignin's content to the quantity of pectin with the hypothesis that 50% of lignin react with sulfuric acid. After this correction, there are always very few protein and lipid except for hemp shiv and flax fines. The cell wall surfaces of the epidermic cell are covered with cutin and suberin (lipids) to reduce water loss from the plants [Chen 2014]. Proteins provide carbon, nitrogen, and sulfur resources for subsequent growth and development of the plant [Herman 1999].

In Tab. 52, these values are compared with these in the scientific literature. For hemp shiv and corn cob, agro-resources from CAVAC (Vendée, France) contain more pectin compared to the composition of lignocellulosic biomass resources in the scientific literature. For hemp shiv, the proportion between pectin, protein and lipid are similar. For rape straw, agro-resource from CAVAC (Vendée, France) contains less pectin and more protein and lipid compared to the composition of lignocellulosic biomass resources in the scientific literature. Like for the content of cellulose, hemicellulose, lignin, soluble and ash, the compositions differ because of the area of production, the weather and the maturity of the plant [Kymäläinen 2008; Vignon 1995].

3.2 Physical characterization

Thermal conductivity

Tab. 53 and Fig. 99 summarize the thermal conductivity versus bulk density at (23°C, dry state) of all aggregates. For each aggregate, the coefficient of variation is lower than 5% as well for bulk density as for thermal conductivity. This induces high confidence in the results. The thermal conductivity ranges from 0.045 to 0.093 W/(m.K) for bulk density ranging from 30 to 392 kg/m^3. Globally, the thermal conductivity increases linearly with bulk density. Corn cob shows much higher thermal conductivity than other aggregates due to much higher bulk density. Indeed, the thermal conductivity of corn cob is 0.093 W/(m.K) when it ranges from 0.045 to 0.058 W/(m.K) for other aggregates. For a given raw material, the discrepancy between thermal conductivity of shiv obtained with several grid size is low (coefficient of variation lower than 4% whatever the raw material) even if the discrepancy between bulk density is high (up to 30%). Thus, the thermal conductivity depends on raw material too. Wheat straw show the lowest thermal conductivity, about 0.045 W/(m.K). Rape straw show slightly higher values than wheat straw, about 0.05 W/(m.K). Flax shiv and hemp shiv show similar values of thermal conductivity, about 0.54 W/(m.K). Finally, the thermal conductivity of fines is higher than the thermal conductivity of shiv (0.058 W/(m.K) for flax fines).

Tab. 53: Thermal conductivity versus bulk density at (23°C, dry state)

Raw materials		Hemp shiv G7	Hemp shiv G8	Hemp shiv G14	Hemp shiv fines	Flax shiv G7	Flax shiv G8	Flax shiv G12	Flax shiv G14	Flax shiv fines	Rape straw G7	Rape straw G8	Rape straw G14	Wheat straw G7	Wheat straw G8	Wheat straw G12	Wheat straw G14	Corn Cob
Bulk density (kg/m^3)	Av.	104.01	87.89	97.36	133.21	111.23	129.91	93.69	90.72	140.30	88.26	78.71	73.26	53.92	49.70	29.69	31.23	392.44
	σ	0.05	0.62	0.44	4.24	0.04	3.05	1.48	0.06	3.26	0.30	2.13	0.11	0.36	2.35	1.20	0.07	2.38
	CoV	0.04%	0.71%	0.45%	3.19%	0.03%	2.35%	1.58%	0.06%	2.32%	0.34%	2.71%	0.15%	0.66%	4.73%	4.04%	0.24%	0.61%
Thermal conductivity (W/(m.K))	Av.	0.0543	0.0530	0.0532	0.0543	0.0540	0.0577	0.0534	0.0531	0.0575	0.0499	0.0497	0.0499	0.0457	0.0457	0.0446	0.0451	0.0926
	σ	0.0008	0.0011	0.0008	0.0010	0.0013	0.0013	0.0022	0.0006	0.0011	0.0006	0.0006	0.0014	0.0009	0.0003	0.0005	0.0002	0.0017
	CoV	1.55%	2.11%	1.42%	1.82%	2.48%	2.33%	4.19%	1.11%	2.00%	1.26%	1.24%	2.75%	2.07%	0.68%	1.20%	0.46%	1.86%

Tab. 54: Thermal conductivity of agro-aggregates from literature

Aggregate	Conditioning	Bulk density (kg/m^3)	Thermal conductivity (W/(m.K))	Reference
Hemp shiv	-	110	0.048	[Cerezo 2005]
Hemp shiv	-	155	0.058	[Cerezo 2005]
0/2.5 Hemp shiv	10°C, air dry material	-	0.057	[Balčiūnas 2016]
2.5/5 Hemp shiv	10°C, air dry material	-	0.055	[Balčiūnas 2016]
5/10 Hemp shiv	10°C, air dry material	-	0.057	[Balčiūnas 2016]
10/20 Hemp shiv	10°C, air dry material	-	0.062	[Balčiūnas 2016]
0/20 Hemp shiv	10°C, air dry material	-	0.056	[Balčiūnas 2016]
Hemp shiv	20°C, dry state	-	0.050	[Rahim 2016]
Hemp shiv	30°C, dry state	-	0.052	[Rahim 2016]
Flax shiv	20°C, dry state	-	0.042	[Rahim 2016]
Flax shiv	30°C, dry state	-	0.044	[Rahim 2016]
Rape straw	20°C, dry state	-	0.047	[Rahim 2016]
Rape straw	30°C, dry state	-	0.049	[Rahim 2016]

Tab. 55: Moisture Buffer Value in adsorption, desorption and average - average value, standard deviation and coefficient of variation between the three samples of a given aggregate

Raw materials		Hemp shiv				Flax shiv					Rape straw			Wheat straw				Corn Cob
		G7	G8	G14	fines	G7	G8	G12	G14	fines	G7	G8	G14	G7	G8	G12	G14	
Bulk density after stabilization at 23°C and 50% RH (kg/m³)	Av.	118.23	101.03	112.80	151.19	121.07	140.49	111.33	109.37	157.80	109.54	84.75	90.95	68.44	58.94	37.37	38.36	405.68
	σ	2.39	0.00	2.11	0.00	3.69	0.00	0.00	1.46	0.00	1.66	0.00	1.01	8.14	0.00	0.00	0.54	6.39
	CoV	2.03%	0.00%	1.87%	0.00%	3.05%	0.00%	0.00%	1.33%	0.00%	1.52%	0.00%	1.11%	11.89%	0.00%	0.01%	1.41%	1.58%
MBV Ads. (g/(m².%RH))	Av.	2.26	2.02	2.26	2.23	2.25	2.12	2.15	2.36	2.46	2.21	2.16	2.23	1.88	1.95	1.87	1.95	2.98
	σ	0.04	0.03	0.09	0.07	0.08	0.04	0.07	0.23	0.05	0.06	0.03	0.06	0.03	0.02	0.07	0.18	0.16
	CoV	1.90%	1.45%	3.76%	3.13%	3.37%	1.72%	3.29%	9.85%	1.92%	2.59%	1.29%	2.75%	1.62%	1.00%	3.90%	9.39%	5.36%
MBV Des. (g/(m².%RH))	Av.	2.32	2.12	2.28	2.32	2.30	2.31	2.28	2.36	2.55	2.24	2.26	2.26	1.89	1.99	1.88	1.92	3.23
	σ	0.04	0.03	0.09	0.06	0.08	0.04	0.06	0.22	0.05	0.06	0.02	0.05	0.03	0.02	0.06	0.19	0.15
	CoV	1.89%	1.57%	3.89%	2.73%	3.36%	1.59%	2.61%	9.46%	1.86%	2.61%	0.88%	2.22%	1.77%	1.14%	3.31%	9.66%	4.63%
MBV Av. (g/(m².%RH))	Av.	2.29	2.07	2.27	2.27	2.27	2.21	2.21	2.36	2.50	2.22	2.21	2.25	1.88	1.97	1.88	1.94	3.11
	σ	0.04	0.03	0.09	0.07	0.07	0.04	0.07	0.23	0.05	0.06	0.02	0.05	0.03	0.02	0.07	0.18	0.15
	CoV	1.79%	1.51%	3.82%	2.92%	3.25%	1.65%	2.94%	9.58%	1.89%	2.56%	1.02%	2.45%	1.66%	1.03%	3.52%	9.40%	4.93%

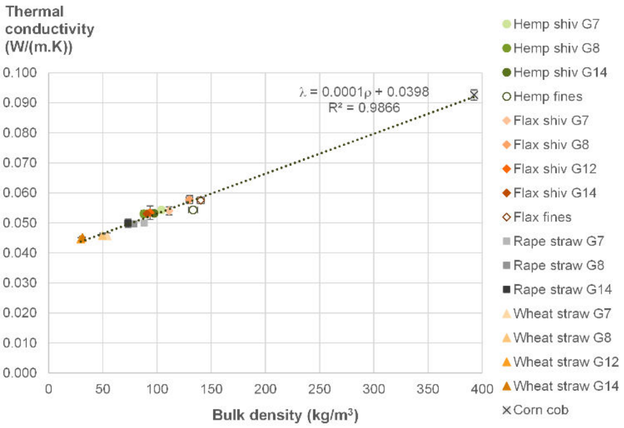

Fig. 99: Thermal conductivity versus bulk density at (23°C, dry state)

Tab. 54 summarizes thermal conductivities of agro-aggregates found in literature. The thermal conductivities of hemp shiv are in the range of bibliography. They are about 5 % higher than values found in [Rahim 2016] and 5 % lower than values given in [Balčiūnas 2016]. For rape straw, the values of thermal conductivity are close to the values found in literature too.

They are about 5 % higher than the value given in [Rahim 2016]. For flax shiv, there is more discrepancy with bibliography.

Actually, the thermal conductivity of flax shiv given in [Rahim 2016] is 22 % lower than the value found here. However, in [Rahim 2016], a self-consistent scheme is used to model the thermal conductivity of bio-based concrete. Experimental data and modelling are in good agreement for hemp concrete and flax concrete and are more scattered for flax concrete. According the authors, this can be explained by the simplified description of the geometrical model. This may also come from the value of thermal conductivity of flax shiv which can be underestimated.

Moisture Buffer Value

Tab. 55 and Fig. 100 give the moisture buffer value for each type of aggregates. Considering all agro-resources, the MBV increases with bulk density. Tab. 55 also gives the average MBV of a given agro resource (from the results obtained on different grid sizes). For a given agro-resource, the results obtained with the different grid sizes are close, the coefficient of variation is low.

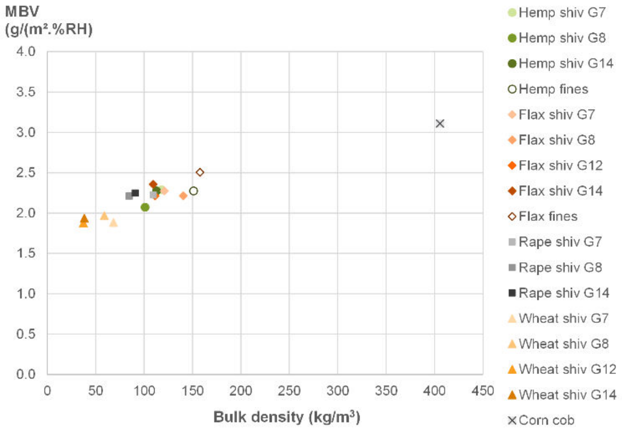

Fig. 100: Moisture Buffer Value versus density

Wheat straw has the smallest MBV, ranging from 1.88 to 1.97 g/(m².%RH). According the classification of the Nordtest project [Rode 2005], it is a good hygric regulator (MBV between 1 and 2 g/(m².%RH)).

Hemp shiv, rape straw and flax shiv show similar MBV ranging from 2.07 to 2.36 g/(m².%RH), with average values about 2.21 to 2.26 g/(m².%RH), According the classification of the Nordtest project, they are excellent hygric regulator (MBV higher than 2 g/(m².%RH)).

Corn cob shows the highest performances with MBV of 3.11 g/(m².%RH).

All these aggregates are very interesting on moisture buffering capacity point of view.

4 CONCLUSIONS

The building industry is one of those fields in which the agro-resources' by-product can have an important role as a bio-based construction material. Substantial economic and environmental benefits can result from the adoption of this solution.

This study considers five agro-resources (hemp, flax, rape, wheat and shiv) which are processed with several grading.

The chemical investigation shows that there are large differences in the chemical composition between these lignocellulosic materials. The high cellulose, hemicellulose and lignin content should allow using such resources as gluing materials or raw material to produce green binder.

The physical characterization shows that all aggregates are light. On a general way, this gives them low thermal conductivity and high moisture buffer value.

Hemp shiv, flax shiv, rape straw and wheat straw have a low thermal conductivity (lower or equal to 0.093 W/(m.K)) and are all excellent hygric regulators (MBV higher than or equal to 1.88 g/(m².%RH), depending on raw materials). However, when the thermal conductivity decreases, the moisture buffer value decreases and vice-versa. Such bio-based aggregates can thus be used to produce thermal insulating products or indoor facing panels (like partition walls or ceiling), coupling them with mineral or green binders.

Hemp fines and flax fines also show high hygrothermal performances. Regarding their particle sizes, these materials should be used as load to produce plaster.

Finally, corn cob shows the highest performances on moisture buffering point of view. This aggregate would be very interesting to be used to produce indoor facing panels (the best MBV) and may be sound-insulating material (thanks to its specific geometric shape and its high density). Such quality need to be investigated further.

Further research is still required to qualify the durability and the fire resistance of these aggregates and to study other properties such as the mechanical ones.

5 ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 636835 – The authors would like to thank them.

CAVAC, industrial partner of the ISOBIO project, is gratefully acknowledged by the authors for providing raw materials.

Thanks are due to Tony Hautecoeur, Yolande Jaguelin (Van Soest analysis) and Stephane Freslon (UV-visible spectrophotometer).

6 REFERENCES

[Amziane 2017] Amziane, S.; Collet, F.; Lawrence, M.; Picandet, V. et al; Bio-aggregates Based Building Materials, RILEM State-of-the-Art Reports, Springer Netherlands, 2017, ISBN 978-94-024-1031-0.

[Balčiūnas 2016] Balčiūnas, G.; Žvironaitė, J.; Vėjelis, S.; Jagniatinskis, A. et al; Ecological, thermal and acoustical insulating composite from hemp shives and sapropel binder, Industrial Crops and Products, 2016, 91, 286–294, ISSN 09266690.

[Cappelletto 2001] Cappelletto, P.; Brizzi, M.; Mongardini, F.; Barberi, B. et al; Italy-grown hemp: yield, composition and cannabinoid content, Industrial Crops and Products, 2001, 13, 2, 101–113, ISSN 0926-6690.

[Cerezo 2005] Cerezo, V.; Propriété mécanique thermiques et acoustiques d'un matériau à base de particules végétales : Approche expérimentale et modélisation théorique, Ecole Nationale des Travaux Publics de l'Etat, Institut National des Sciences Appliquées de Lyon, 2005.

[Contreras 1999] Contreras, L.; Gutièrrez Chavez, D.; Valdivia Macedo, I.; Govea Casares, R. et al; Two techniques for measuring neutral detergent (NDF) and acid detergent fibers (ADF) in forages and by-products.pdf, Archivos de Zootecnia, 1999 , 48, 183, 351–354.

[Chen 2014] Chen, H.; Chemical composition and structure of natural lignocellulose, Biotechnology of lignocellulose, 2014, Springer, 25–71.

[Carrier 2011] Carrier, M.; Loppinet-Serani, A.; Denux, D.; Lasnier, J.-M. et al; Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass, Biomass and Bioenergy, 2011, 35, 1, 298–307, ISSN 09619534.

[Dubois 1956] Dubois, M.; Gilles, K.A.; Hamilton, J.K.; Rebers, P. A. T. et al; Colorimetric method for determination of sugars and related substances, Analytical chemistry, 1956 , 28, 3, 350–356.

[Dyer 1999] Dyer, T.J.; Elucidating the formation and chemistry of chromophores during kraft pulping, Location: Atlanta, Georgia, University of Wisconsin-Stevens Point, 1999.

[Evon 2008] Evon, P.; Nouveau procédé de bioraffinage du tournesol plante entière par fractionnement thermo-mécano-chimique en extrudeur bi-vis: étude de l'extraction aqueuse des lipides et de la mise en forme du raffinat en agromatériaux par thermomoulage, Location: Toulouse, France, 2008.

[Fava 2015] Fava, F.; Totaro, G.; Diels, L.; Reis, M. et al; Biowaste biorefinery in Europe: opportunities and research & development needs, New Biotechnology, 2015, 32, 1, 100–108, ISSN 18716784.

[Gao 2014] Gao, X.; Kumar, R.; Wyman, C.E.; Fast hemicellulose quantification via a simple one-step acid hydrolysis, Biotechnology and Bioengineering, 2014, 111, 6, 1088–1096, ISSN 1097-0290.

[Godin 2010] Godin, B.; Ghysel, F.; Agneessens, R.; Gofflot, S. et al; Détermination de la cellulose, des hémicelluloses, de la lignine et des cendres dans diverses cultures lignocellulosiques dédiées à la production de bioéthanol de deuxième génération, Biotechnol. Agron. Soc. Environ., 2010, 14, S2, 549–560.

[Greenhalf 2012] Greenhalf, C.E.; Nowakowski, D.J.; Bridgwater, A.V.; Titiloye, J. et al; Thermochemical characterisation of straws and high yielding perennial grasses, Industrial Crops and Products, 2012, 36, 1, 449–459, ISSN 09266690.

[Hameed 2014] Hameed, M.R.; Contribution of metallic fibers on the performance of reinforced concrete, Location: Toulouse, France, 2014.

[Herman 1999] Herman, E.M.; Larkins, B.A.; Protein storage bodies and vacuoles, The Plant Cell, 1999, 11, 4, 601–613.

[Jeong 2011] Jeong, T.S.; Oh, K.K.; Optimization of fermentable sugar production from rape straw through hydrothermal acid pretreatment, Bioresource Technology, 2011, 102, 19, 9261–9266, ISSN 09608524.

[Kymäläinen 2008] Kymäläinen, H.-R.; Sjöberg, A.-M.; Flax and hemp fibres as raw materials for thermal insulations, Building and Environment, 2008, 43, 7, 1261–1269, ISSN 03601323.

[Pointner 2014] Pointner, M.; Kuttner, P.; Obrlik, T.; Jager, A. et al; Composition of corncobs as a substrate for fermentation of biofuels, Agronomy Research, 2014, 12, 2, 391–396.

[Rahim 2016] Rahim, M.; Douzane, O.; Tran Le, A.D.; Promis, G. et al; Effect of moisture and temperature on thermal properties of three bio-based materials, Construction and Building Materials, 2016, 111, 119–127, ISSN 09500618.

[Ross 2010] Ross, K.; Mazza, G.; Characteristics of Lignin from Flax Shives as Affected by Extraction Conditions, International Journal of Molecular Sciences, 2010, 11, 10, 4035–4050, ISSN 1422-0067.

[Rode 2005] Rode, C.; Peuhkuri, R.H.; Mortensen, L.H.; Hansen, K. K. et al; Moisture buffering of building materials, Technical University of Denmark, Department of Civil Engineering, 2005.

[Sain 2002] Sain, M.; Fortier, D.; Flax shives refining, chemical modification and hydrophobisation for paper production, Industrial Crops and Products, 2002, 15, 1, 1–13.

[Sorieul 2016] Sorieul, M.; Dickson, A.; Hill, S.; Pearson, H.; Plant Fibre: Molecular Structure and Biomechanical Properties, of a Complex Living Material, Influencing Its Deconstruction towards a Biobased Composite, Materials, 2016, 9, 8, 618, ISSN 1996-1944.

[Searle 2013] Searle, S.; Malins, C.; Availability of cellulosic residues and wastes in the EU, White paper, 2013, 422.

[Silva 2014] Silva, A.S.; Nunes, C.; Coimbra, M.A.; Guido, L.F.; Composition of pectic polysaccharides in a Portuguese apple (Malus domestica Borkh. cv Bravo de Esmolfe), Scientia Agricola, 2014, 71, 4, 331–336, ISSN 0103-9016.

[Sun 2000] Sun, R.C.; Tomkinson, J.; Essential guides for isolation/purification of polysaccharides, Academic Press: Lond, 2000.

[Van Soest 1991] Van Soest, P.J.; Robertson, J.B.; Lewis, B.A.; Symposium: carbohydrate methodology, metabolism, and nutritional implications in dairy cattle, J. Dairy Sci, 1991, 74, 10, 3583–3597.

[Voragen 2009] Voragen, A.G.J.; Coenen, G.-J.; Verhoef R. P. and Schols H. A.; Pectin, a versatile polysaccharide present in plant cell walls, Structural Chemistry, 2009, 20, 2, 263–275, ISSN 1040-0400, 1572-9001.

[Vignon 1995] Vignon, M.R.; Garcia-Jaldon, C.; Dupeyre, D.; Steam explosion of woody hemp chenevotte, International journal of biological macromolecules, 1995, 17, 6, 395–404.