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Communication

Vegetal Refining and Agrichemistry

The industrial process developed by CIMV is a world first for the manufacture of whitened paper pulp, sulfur free linear lignin and xylose syrup from annual fiber crops and hardwood. This new technology allows the separation without degradation of the three main components, i.e., cellulose, hemicelluloses and lignins, isolated from the vegetable matter. The CIMV process is a biorefinery functioning on a model resembling an oil refinery. The lignins have a linear structure that permits high reactivity with different monomers producing new polymers and new formaldehyde-free adhesive formulations. The *C*-5 sugar syrup can be used to produce additives for animal feeding and chemicals. The pilot plant in operation since 2006, near Reims, has given fully satisfactory results. The CIMV chemical engineering approach, proceeds by the use of classical industrial equipment. This should allow the scale up of the original CIMV concept to result in production at industrial levels in 2009.

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1 Introduction

Since the end of the twentieth century, there has been no real major breakthrough in changes for the industrial paper technology, with respect to the chemical, thermomechanical and mechanical pulp quality. Until recently, limited improvements have been made via the treatment of hardwood and softwood in modern production facilities. Regrettably, the processes used have been restricted in terms of effectiveness and environmental friendliness. Hence, cellulose remains the only part of the wood that has been satisfactorily developed. The resultant hemicelluloses and lignins can be strongly degraded, and they have been used either as a source of energy, in the case of the chemical processes, or were discarded in rivers, in the case of mechanical pulps. Bleaching was usually performed with chlorine derivatives and required large amounts of water, which were returned into the rivers, resulting in this chemical step being an important source of pollution. In addition, the technologies of the twentieth century did not make efficient use of the availability of annual crops to produce pulp, owing to their high silica content, which made it practically impossible to incinerate the black liquor that formed.

The CIMV process [1–9] has been shown to be a real breakthrough that offers a new alternative, since it allows the separation without degradation of all the constituents of the vegetable matter, with exceptional valorization of cellulose, lignins and xylose. It has been shown that silica is not an obstacle, with the use of annual plants and may become a valuable resource as well as the wood. The details of the reactions, chemical operations and chemical analysis are summarized below. These have been reported in the patents and publications referenced [1–11] and are available on the internet.

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2 The CIMV Biorefinery

The process that has been developed is designed for the manufacture of whitened paper pulp, sulfur-free linear lignin and *C*-5 sugar syrup from annual fiber plants. This new technology allows the separation, without degradation, of the three main components of the vegetable matter, i.e., cellulose, hemicelluloses and lignins. CIMV is a vegetable refinery designed to mimic a model oil refinery, Fig. 1.

In the first stage, the vegetal matter is treated at atmospheric pressure with a mixture of acetic acid and formic acid, which dissolves lignins and hydrolyses the hemicelluloses into oligo- and monosaccharides with high xylose content. The raw pulp is then filtered, the solvent is removed and the residue is bleached with hydrogen peroxide. The commercial value of the raw pulp is close to that of eucalyptus chemical pulp. The organic acids are then recycled by evaporation from the organic solution. The remaining syrup is then treated with water to precipitate the lignin, which is easily separated. The obtained lignin shows a totally novel linear structure [10, 11], which can be used as a reactant for chemical production of new polymers and composites synthesis. The raw syrup which, without puri-

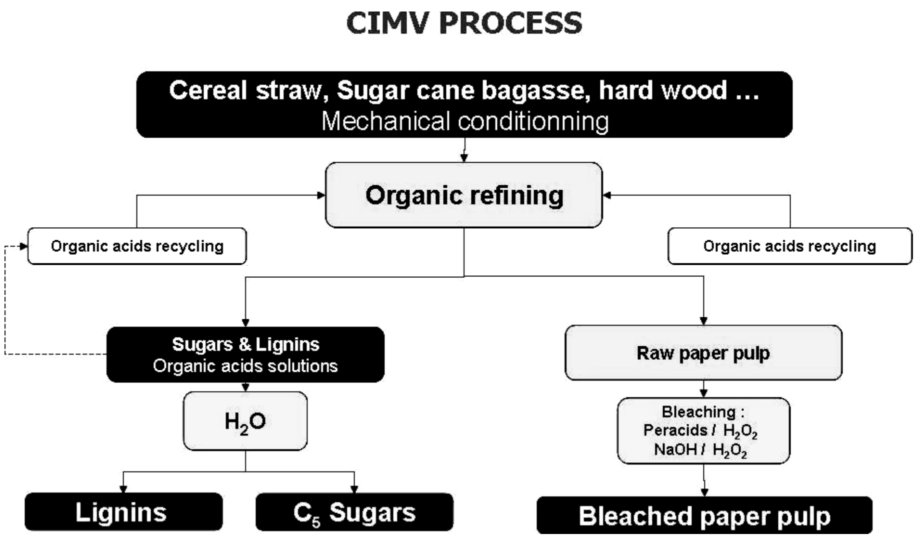


Figure 1. The CIMV process biorefinery.

fication, resembles molasses can be used directly for numerous industrial applications.

3 The Resources

Presently, resinous and hardwoods are the only real sources of pulp production, which ensure more than 97 % of world pulp demands. These natural resources have become expensive, and difficult to access. It has also been proven scientifically that the harvesting of these resources will not sustainable due to the continuous increase in worldwide paper consumption. The alternative uses of annual crops, such as cereal straws or sugar cane bagasse, which are easily obtainable at lower costs, are extremely suitable replacements. This is unavoidable since the collection of the crop resources has been extremely easy to set up. Furthermore, the producers are well organized and have the scientific knowledge and understanding of the benefit they will make by releasing them for exploitation, through the CIMV industrial process.

3.1 Cereal Straws

In the majority of the European countries, 60 % of the available cereal straws are burned or buried. The collection of the cereal straws is easy and well integrated with the collection of grain. In addition, this skill is very well organized and structured. Hundreds of millions of tons of cereal straws are immediately available in the European Union, and their harvesting will cause no agronomic damage to soils. A comparable situation prevails in the USA, Canada, Australia and Argentina and in the countries of Eastern Europe.

In Asia, the rice straw resource is immense, but very poorly exploited for pulp production, due to non-compliance with the current industrial techniques. This creates insurmountable problems arising from the great quantity of silica present in such straw. Such a method would generate enormous pollution of the rivers, particularly in China and India. The CIMV process is the first industrial-scale technology that can use straws without generating this particular type of pollution, and this opens enormous new ventures and prospects for the process.

3.2 Sugar Cane and Sweet Sorghum Bagasse

Australia, Brazil, China, India, the USA, the Caribbean Islands are some of the principal countries that have a strong and a broad knowledge with regard to the sugar cane industry. In these countries, the average size of the manufacturing units makes it possible to process surplus bagasse for a CIMV unit without any major problem. Consequently, the introduction of a CIMV production facility appears to be the perfect complement to the sugar refinery. This production facility will even permit a technical solution to the excess of bagasse obtained from the sugar refinery, which can be used in parallel for the optimization of the shutter energy.

In these geographical areas, sweet sorghum can be produced in rotation with sugar cane and collected every other year. This option should be considered with respect to two very favorable characteristics, which are:

- The use of the existing industrial methodology, without modification, for harvesting and extraction of the sugar and storage of bagasse.
- The exceptional paper quality of sweet sorghum fibers.

3.3 Hardwood

The technology works very well with hardwood, in particular birch. The pulp obtained has the same chemical and physical characteristics as those of Kraft pulp. The lignins show the same linear structure as straw and the xylose syrup is very suitable for xylitol production.

4 The Commercial Products

4.1 Cellulose

In order to appreciate the opportunities, it should be noted that France alone, currently imports almost 700,000 tonne of hardwood pulp, primarily eucalyptus, which comes mainly from Brazil. On the scale of Western Europe, these figures can be multiplied by 6- or 7-fold, and are measured in millions of tons on a worldwide scale. The CIMV pulps have properties identical to those of hardwood pulps, in particular of eucalyptus, and thus, can easily be substituted for them. As already mentioned, the CIMV produced pulp has the same qualities as eucalyptus pulp, and this fact opens new horizons for marketing and commercial uses. Due to its intrinsic qualities of this cellulose, e.g., rigidity and opacity, it is a good material for puffing pulps, which are the most expensive on the market. These advantages will continue to escalate in importance in a world increasingly sensitive to environmental constraints.

The mixture of CIMV pulps of sugar cane or sweet sorghum bagasses with those resulting from wheat straw should allow the marketing of the first standard writing impression paper, which will be manufactured without wood. These products will very quickly penetrate the traditional markets where the commercial concerns are in search of this type of paper. Owing to the fact that the CIMV pulp does not contain any resin, current substitution of some plastic packing materials with paper will ensure a great dissemination of the pulp. In addition, the CIMV pulps are immediately exploitable in the world, due to the fact that they are nonflammable, whereas other commercial pulps have to be submitted to rigorous expensive transformations to rid them of the resin that they contain, an operation made essential due to their potential for causing fire. The straw pulps obtained by the CIMV process have the characteristics outlined in Tab. 1.

Table 1. The CIMV wheat pulps characteristics.

SR	30–35
Density	1.2–1.3
Breaking length (m)	4800–5000
Bursting index (kPa m^2/g)	2.6–2.8
Tearing index (mN m^2/g)	2.9–3.1
Opacity (%)	91–93
Permeability (cm^3/m^2)	0.52–0.54
Brightness	84–86

It is noteworthy to mention that the manufacture of paper pulp is not the only industrial opening for CIMV. Therefore, the pulp profit has a larger flexibility of adaptation to the market, which is much higher than the current coexisting productions entirely dedicated to paper.

4.2 Lignins

It has been clearly demonstrated that the CIMV lignins are linear polymers of great interest for a large range of organic materials [9–11]. This astonishing result is due simply to the very soft conditions of extraction, which avoid the reticulation and degradation of the phenolic oligomers.

The lignin extracted from wheat straw is a brown powder with a density of 0.9 g/cm^3 (1.30 g/cm^3 in the condensed state). The medium particle size is ca. 2 microns. The molar mass distribution curves of lignin, obtained by size exclusion chromatography show molecular weights between 1000–1500 g/mol, which agrees very well with the results obtained by the atmospheric pressure photoionization (APPI) tandem mass spectrometry analysis [11]. Lignin is soluble in cyclic ethers such as dioxane or tetrahydrofurane and also in acidic and basic organic media. The qualitative and quantitative analysis of hydroxyl groups by means of propenylation gives the results reported in Tab. 2.

Table 2. Hydroxyl groups in straw lignins.

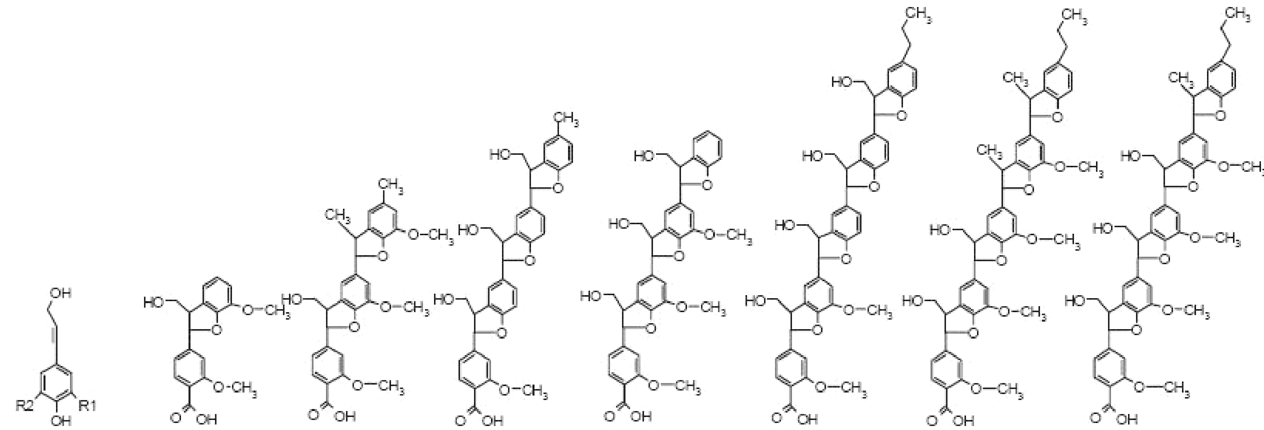
	Formyl[a]	Acetyl[a]	Hydroxyl[a]	Total
OH (aliphatic and phenolic)	0.6	0.5	2.9	4
OH phenolic	0.2	0.05	0.85	1.1
OH aliphatic	0.4	0.45	2.05	2.9

[a] mmol/g of lignin.

The presence of the formyl and acetyl groups results from the conditions of extraction, i.e., acetic acid and formic acid media. Thermal degradation of these lignins occurs between 185–210 °C. A previous investigation on the lignin structures of wheat straw by mass spectrometry [9–11] indicated that lignin polymers are composed of a mixture of linear polycondensed coniferyl units forming the native polymers, Fig. 2. These structures are in equilibrium in acetic acid/formic acid/water media with the open form apparent, Fig. 3.This type of organosolv lignins has a great future in the polymeric material industries as summarized recently by Lora and Glasser [12]. Further development requires production on the industrial scale of these types of lignins. Currently, there are no organosolv lignins on the market. It is an objective is to produce these lignins on an industrial scale in 2009 to substitute for the corresponding products produced by the petrochemical industry to open the way for future agrichemistry.

Among the great number of possible industrial developments based on organosolv lignins, the following are extremely noteworthy:

- The use of organosolv lignins as a substitute for phenolic powder resins as the binder in the manufacture of friction products.
- Utilization in oriented strand board (OSB), which is the dominant construction wood panel in North America. The strands are bound by phenolic resins in powder or liquid form. A partial replacement with ca. 25 % of organosolv lignins gives excellent results. In the same way, the addition of organosolv lignins with isocyanate binders for wood particles results in improved performance with cost benefits.
- Incorporation in polyurethane foams at levels of 30–40 %, improves the response on exposure to elevated temperature and humidity conditions.
- The use of organosolv lignins in epoxy resins, e.g., epoxy resins that contained ca. 50 % of sulfur-free lignins were successfully prepared and used for the production of printed circuit board resins.
- The ability for organosolv sulfur-free lignin to make a significant impact in these areas depends on its availability in in-

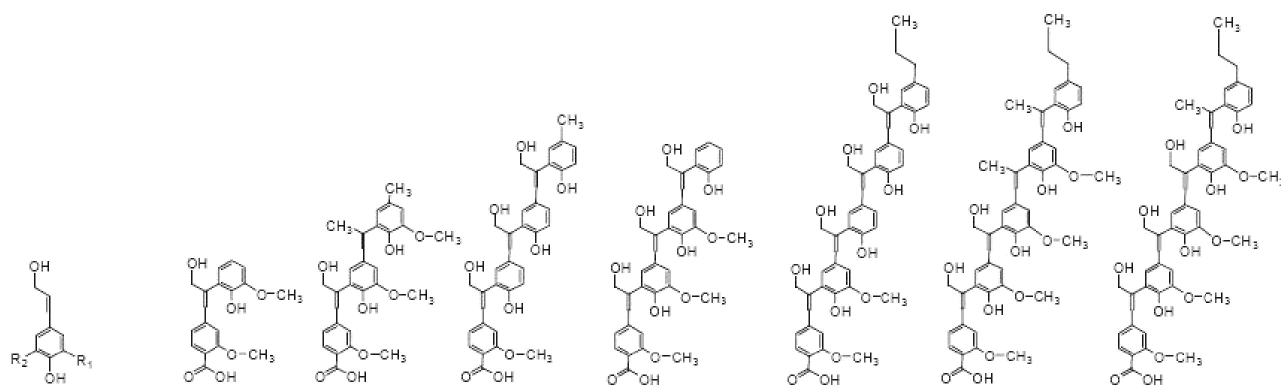


1A: $R_1=OCH_3$ R2=H 2:$C_{18}H_{18}O_6$ M.Wt.=330.11 3:$C_{29}H_{30}O_8$ M.Wt.=506.19 4:$C_{36}H_{34}O_9$ M.Wt.=610.22 5:$C_{37}H_{36}O_{11}$ M.Wt.=656.22 6:$C_{48}H_{48}O_{12}$ M.Wt.=816.31 7:$C_{50}H_{52}O_{12}$ M.Wt.=844.34 8:$C_{50}H_{52}O_{13}$ M.Wt.=860.34

1B: $R_1=R_2=OCH_3$

1C: $R_1=R_2=H$

Figure 2. Wheat straw lignins structures [9–11].



1A : R_1 = OCH_3 R_2 = H 2 : $C_{18}H_{18}O_6$ M.Wt. = 330.11 3 : $C_{29}H_{30}O_8$ M.Wt. = 506.19 4 : $C_{36}H_{34}O_9$ M.Wt. = 610.22 5 : $C_{37}H_{36}O_{11}$ M.Wt. = 656.22 6 : $C_{48}H_{48}O_{12}$ M.Wt. = 816.31 7 : $C_{50}H_{52}O_{12}$ M.Wt. = 844.34 8 : $C_{50}H_{52}O_{13}$ M.Wt. = 860.34

1B : R_1 = R_2 = OCH_3

1C : R_1 = R_2 = H

Figure 3. Wheat straw lignins in acetic acid/formic acid/water media.

dustrial quantities as a high purity product. The aim of this review is to spread a new movement, and to lay the corner stone for the production of improved pulps and associated products including lignins and xylitol by using greener technologies such as the CIMV process.

4.3 Xylose and Derivatives

Hemicelluloses constitute, with lignins, the organic binders of cellulose fibers in plants. The composite that results provides the structural aspect of plants. The action of formic acid and acetic acid transforms them into a mixture of monomeric sugars by solvation followed by hydrolysis of the glycosidic bond connections of the monomeric sugars constituting these hemicelluloses. These are mainly xylose in the case of cereal straws, hardwood and more general annual crops.

The wheat straw sugar syrup characterization gives the results outlined in Tab. 3. The *C*-5 sugars are produced under advantageous economic conditions, thanks to the valorization of all of the components of the raw material. The *C*-5 sugars do not currently have large industrial openings, because of associated pollution and the prohibitive cost of extraction they incur by current techniques. Xylose is either produced directly in small quantities by expensive processes or it is extracted from the bisulphite black liquors. This associated high production cost, limits the use with respect to this particular commodity, which produces xylitol. Xylitol has several applications in the food sector as a sweetener having two particular characteristics, i.e., it is at the same time acariogenic, and is therefore, used in the manufacture of chewing-gums and it can be assimilated by the body, without the use of insulin.

Since the production of crystalline xylose is an expensive process, it is usually very difficult to identify commercial outlets for

Table 3. Sugar syrup contents.

Sugar syrup components	% (dry matter)
Mineral Matter	19
Lipids	3.8
Proteins	6.3
Tanins	5.5
Furfural	0.02
HMF	Traces
Free xylose	11.8
Free arabinose	6.25
Free glucose	0
Total free sugars	**18**
Bounded Xylose	27
Bounded Arabinose	2.75
Bounded glucose	3.25
Total bounded sugars	**33**
Total sugars	**51 % (with 38.8 % of xylose)**

this product, hence limiting its distribution. As with all products, the possible outlets for xylose depend directly on the price at which it can be marketed by the companies which produce it.

In the case of a CIMV biorefinery, the situation of co-production of xylose makes it possible to consider a very profitable valorization through the following four industrial points which are the corner stone of a future agrichemical industry:

- Production of xylitol at a price much lower than the current price in order to enhance possible applications, and consequently, the existing production, i.e., ca. 25,000 tons/year worldwide.
- Production of furfural, furfurylic alcohol and furan resins, i.e., current world market of 120,000 tons, with a potential of more than one million tons.
- Use as a fermentation substrate for the industrial production of pro-octane ethanol biofuel additives.
- Use of vegetal proteins as a tanning agent instead of formaldehyde in animal feeding.

4.4 The CIMV Bioethanol/Lignin Biorefinery

The production of alcohol for biofuel use from maize and wheat is, at present, endangered by the increase in the price of grains due to competition with the foodstuff sector for the use of flour and starch. A large number of people and companies are looking today on what is known as second generation alcohol production from lignocellulosic materials. The main difficulties in the production of second generation alcohol are the low efficiency of the enzymes used to convert the polysaccharides into sugars before fermentation.

By comparison with the classical steam explosion technique, the CIMV technology offers an original and very efficient pretreatment of the corresponding lignocellulosic raw material such as wood, straw, etc. The method gives superior results in terms of yield, selectivity and pollution control [13]. A simplified flowsheet summarizing the operations in the biorefinery is shown in Fig. 4.

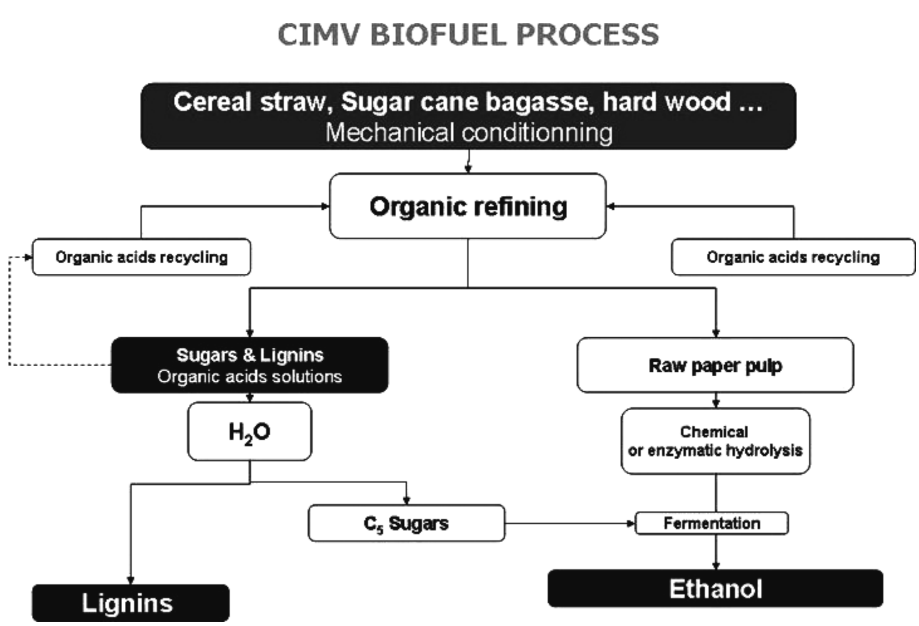


Figure 4. The CIMV bioethanol/lignins biorefinery.

5 The Pilot Plant

The CIMV pilot factory built on the industrial site of the ARD Company in Pomacle, close to Reims in the North East of France was designed to continuously treat 100 kg of dry vegetable matter per hour. The pilot plant is operational since January 2006 with fully satisfactory results. The data reported in Tabs. 1–3 comes from cellulose, lignins and sugar syrups obtained in large quantities with the pilot plant.

6 The Construction of the First Factory

The CIMV biorefinery is a completely new concept. Initially, efforts focused on scaling up from the laboratory to the pilot plant, and are now focusing on the second scaling up to the first CIMV factory. The factory will avail of the knowledge obtained from the different chemical engineering operations, and consequently, use the classical and well-known equipment coming from different industrial processes, such as:

- The stock preparation of straw will employ equipment well known to the hemp and flax industry.
- The acetic acid/formic acid/water extraction and the delignification of the raw pulp will be carried out in a reactor very similar to the conveyor belt reactor used to extract sugar by diffusion from sugar beet and sugar cane.
- The pulp desolvation will be carried out in evaporators that are similar to those used for the desolvation of rapeseed and soya meals.
- The pulp bleaching line is the same as a wood pulp line.
- The others equipment, i.e., evaporators, concentrators, filters and pumps, etc. come from the chemical industry.

The construction of the first biorefinery for this process by the CIMV Company, as a joint venture with the cereal cooperative Champagne Cereals, in Loisy sur Marne, near Vitry le Francois in the Champagne Ardennes region, is progressing. The factory is designed to treat 150,000 tons of wheat and barley straws annually and will start production in October 2009.

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