

Technical and Economic Overview of the Cellulignin Production Process.

Paolo Gronchi^{a*}, Mauro Delfanti^b, Gianmarco Rivoli^c

^aPolitecnico di Milano, Chemistry, Material and Engineering Chemistry Dept. P.zza Leonardo Da Vinci 32, 20133 Milano

^bEnergy and Safety consultant, Via Monte Suello, 5, 20133 Milano,

^cEnergy and Environment consultant, Via Lomellina, 50, 20133 Milano

paolo.gronchi@polimi.it

This paper analyses the chemical conversion process of biomass based on a diluted acid hydrolysis step, the Biomass Energy Process (BEM). The discussion starts from the technical point of view on the base of information reported literature, experimental laboratory analyses and pilot plant tests and then the authors tentatively explore the energy related costs of the process giving a comparison of the biomass derived solid fuel and fossil fuels. An evaluation of the product (cellulignin powder compacted into briquettes) and considered as a fuel and other energy sources from fossil resources like oil, natural gas and coal, is reported considering the energy density and energy cost. The main technical feature of the process is the conversion of almost every type of bug wood biomass with a large range of chemical and physical characteristics. The hydrolysis step determines the energy price and the threshold cost of the cellulignin is calculated at 60-70 euro/t about over which the NG energy is preferable. Environmental concerns can be however considered.

1. Introduction

As far as future biomass conversion is concerned, the choice of feedstock is a critical consideration. Considering the food needs for the world's growing population it is necessary to exploit cellulose, straw and sugar cane for bioethanol and pure cellulose or algae for fuel productions assuring a CO₂ sequestration capacity over 50% of bio-fuels calculated using a structured LCA analysis. By 2017 this limit will raise up to 60%. These determinations deeply change the process of the biomass conversion whose first step is the solubilisation or depolymerisation of the lignocellulose biomass. While on the side of the bioethanol production the almost mandatory first step is the fermentation step, on the side of the conversion for biofuels or energy production processes with new solvent have to be explored that may be useful in order to perform chemical transformation. The cellulignin production process, the object of the present work, establishes an alternative chemical process respect to the fermentation, chemical dissolution or gasification processes. This process does not use solvent (only water) and its heart is the diluted acid hydrolysis. The pre-hydrolysis step (Pinatti 1999; Pinatti 2003; Pinatti 2005) starts the full biomass exploiting process generating two products: a solid cellulignin fuel (CL) and acid muds containing chemicals (furfural, alcohol or xylitol). The most important debate is however the economic convenience of the process.

2. The BEM process

The BEM process aims at the greatest and efficient conversion of any sort of biomass source to renewable energy through the production of intermediate and final materials with constant properties whichever could be complexity of the biomass. The process design aims at assuring compatibility of the energy cost from biomass source and chemical used products. The process plant is intensive and works the biomass near the harvesting site then it is small and easy positioned, owing to the relevance of the transport costs.

As above affirmed the heart of the process is the pre-hydrolysis that generates two products: fine powdered cellulignin fuel (CL) and biomass derived chemicals (furfural, alcohol or xylitol). The flow chart of the process is reported in Figure 1. Pre-hydrolysis of bug wood produces cellulignin, soft material with large surface area looking as a fine powder, which can be used to make briquettes.

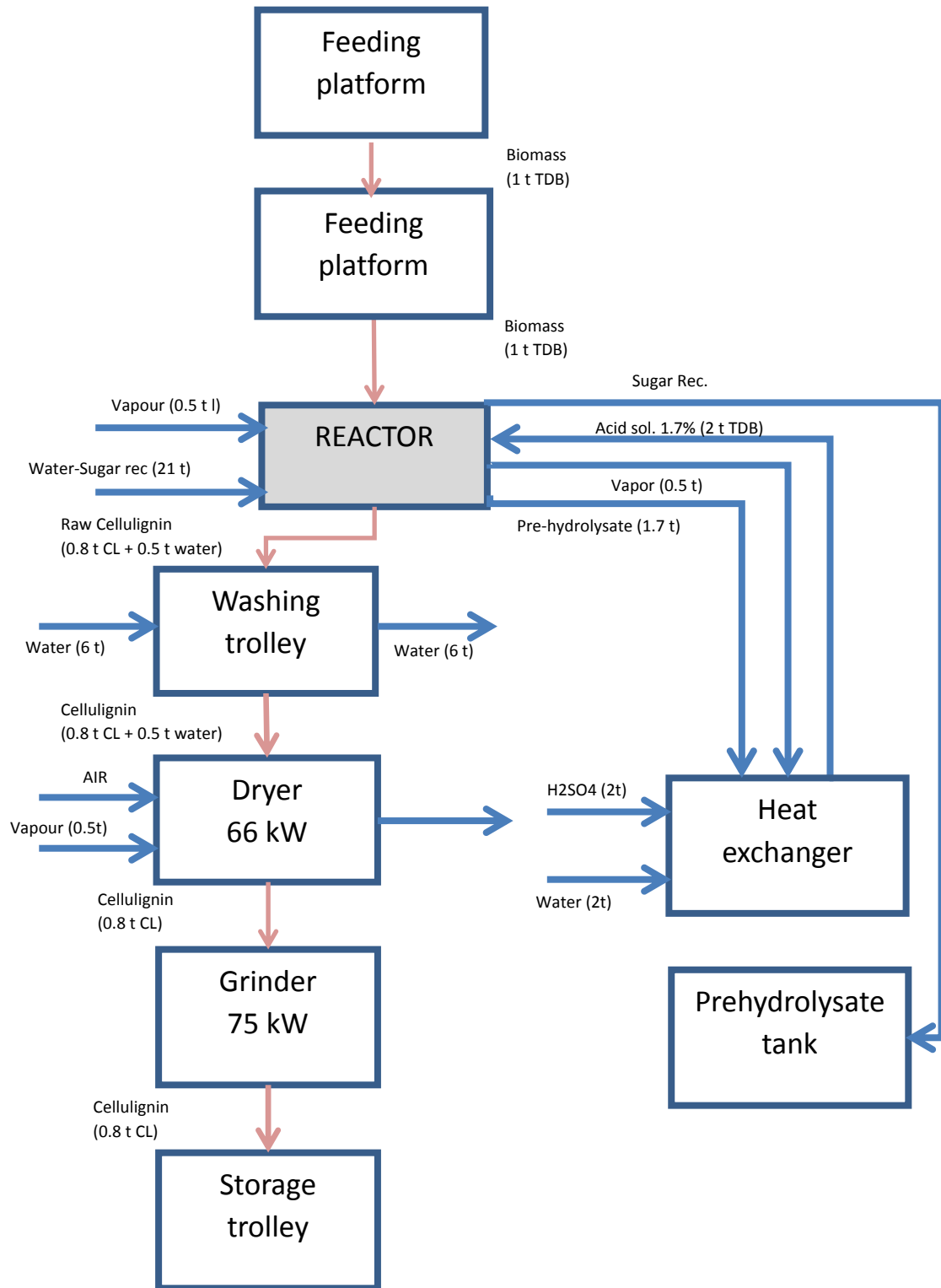


Figure 1. Process flow chart (Pinatti, 1999)

CL can be produced in two grades, the first with potable water (0.2% ash, K + Na <100 ppm) and the second with deionised water (0.1% ash, Na + K <25 ppm). These fuels can be used in gas-type turbines with external combustor and cyclone cleaning of the ash and particulates.

Pre-hydrolysis of biomass has several distinct advantages. The process is independent from the initial moisture of the biomass feedstock. Alkaline and ash components are removed at the start of the process by the dilute acid to avoid downstream conversion issues. Water recycling makes the process environmentally sustainable and closed-loop.

Cellulignin can be compacted and shaped into square briquettes so that the bulk and the material densities are the same: 1,250 kg/m³. This results into a specific energy of 23 GJ/m³ which is similar to bituminous coal, 26 GJ/m³, a fossil fuel commodity that is shipped and transported over significant distances.

Both bound and free water are easily drained out during the pre-hydrolysis process, allowing reduced drying, heating and power costs to make briquettes. Pre-hydrolysis dilute acid and washing process reduce the ash levels to less than 0.2 %; potassium and sodium levels decrease to below 100 ppm. This aspect is very important when using biomass, for example, in power production to reduce particulate matter, corrosion and slagging - important elements that impact operating and maintenance costs of equipment.

More important, it allows cellulignin to have significantly less contaminants, making it better suited to develop higher-value processes and enabling its use directly in a gas turbine if turbine material problems are adequately addressed. Ash and alkaline contents can be further reduced if washing is performed with distilled water.

The fine powder produced after grinding can be atomized using a natural gas burner, allowing the substitution of natural gas with cellulignin in many applications.

This is very important as there are limited equipment modifications required for the end user, thereby limited capital cost involved in fuel switching. In addition, cellulignin avoids the many fuel handling issues characteristic of biomass systems. The energy required to grind the cellulignin is low compared to other processes. Cellulignin can be used to make a syngas without the need of a gasifier, eliminating tar issues and facilitating the production of other, more complex, fuels.

The resulting pre-hydrolysate liquor contains furfural (C₅H₄O₂) together with sugars and organic acids, a commodity that sells for 1,000 US\$/t to be used mainly for plastic production. Some HPLC identified organic compounds are reported in Table 1.

Table 1. Products (%) identified by HPLC in the pre-hydrolysate liquor at two levels of temperature after 45 min of acid reaction.

Product	RT/min	%	
		303 K	318 K
Furfurol	3.7	34.85	40.37
Vanilline	15.68	4.58	4.46
Phenol	18.14	10.63	6.11
Benzaldehyde	20.58	12.28	11.09
Benzene-4-hydroxy-2-methoxy cinnamaldehyde	21.48	2.91	2.75
o-phthalic acid	23.78	0.18	0.18
3-(3',5'-dimethoxy-4'-hydroxyphenyl)-E-propenal (Amines)	24.03	2.08	1.52
	32.14	0.82	0.50

3. Cellulignin Briquettes

Biomass can be transported in the form of briquettes. Briquettes avoid some of the disadvantages of conventional wood briquettes. They burn very cleanly, have less ash and inorganic materials, and can be used to replace natural gas in industrial applications. Shipped as high-density briquettes, cellulignin briquettes can easily be used to generate power and heat at the point of use, where they can replace natural gas as a fuel. In addition, bark and branches can be utilized, which allows a large variety of biomass feedstocks. To make conventional briquettes, wood is de-barked and ground up into small fines

and compressed at high pressure into 50 mm diameter or larger briquettes. No binding agent is used as the heat resulting from the compression can be sufficient in most cases to let the lignin bind the material together. The advantage of this method is that it produces a material which is easy to handle and package, and which can be transported economically. For briquetting, the moisture content of the biomass must be below 10 % to 15 %, otherwise drying is required. Briquettes have a high specific density of up to 1,200 kg/m³ and a bulk density of 800 kg/m³. In comparison, bug wood has a bone dry density of 380 kg/m³, a density of 460 kg/m³ at 20 % moisture content, and when chipped the interspatial air decreases the bulk density to less than 230 kg/m³. Biomass briquettes have the following advantages:

- Higher boiler efficiency compared to bulk biomass because of lower moisture content and possibly better conversion rates;
- Reduced loading, unloading, transportation and storage costs;
- Can be economical in some applications depending on feedstock, transportation and manufacturing costs, and are a renewable fuel;
- Less sulphur compared to oil and coal, thereby reducing environmental impact;
- Higher thermal value compared to bulk biomass and much lower ash content compared to bulk biomass and coal;
- Consistent quality;
- Reduced fly ash; as for steam boilers is easier compared to coal, due to higher quantity of volatile matter.
- Conventional wood briquettes have some shortcomings:
 - They cannot withstand direct contact with water;
 - A covered storage facility is required;
 - They require debarking, sizing and potential drying of the biomass, processes that require energy;
 - Precludes the use of branches left over in the forest after logging;
 - The maximum attainable temperature is 1000°C due to the low carbon content limiting their applications, for example, in lime kiln;
 - Burning capacity per unit volume of furnace is low compared to coal; and,
 - Availability in remote regions is not assured all year round unless enough storage is made.

4. Economic survey

The economic survey deeply depends on the biomass harvesting site as the transport costs determine the total price of energy (Tampier, 2006). However, as cellulignin can be rightly considered as an energy source, as it has a heating value between 18 and 20 MJ/kg, depending on the biomass feedstock. Besides it is derived from, and an ignition time less than 20 ms, making it a possible replacement for natural gas for combustion. The CL produced is a fuel composed of cellulose and globulized lignin with a specific surface of about 1.5 to 2.5 m²/g once ground into a fine powder that enhances thermal and biological conversion. The comparison can be made among other energy sources like Electricity, Fuel oil, Coal or NG. Table 2 shows the relative difference in heat densities and the cost of various energy sources: CL has 57 % the energy density of fuel oil and 88% of bituminous coal. The value here reported for cellulignin, 72 €/t from which the energy cost (1.3 c€/kWh) has been calculated, establishes a comparison level. Over this level the cellulignin fuel becomes less convenient than NG source. The cost value takes into account the biomass cost and pre-hydrolysis cost.

Table 2. Energy density and cost comparison. Italy: oil = 100 \$/barrel; NG = 8 \$/MMBTU

Energy sources	Density (kg/m ³)	HHV (MJ/m ³)	Energy density (kJ/kg)	CL energy (%)	Cost (c€/kWh) (100% eff.)	Notes
Electricity					20	
Fuel Oil (l)	980	43	43.9	57	4.5	100 \$/barrel
Bituminous Coal	850	27.7	32.5	88	1.3	5 \$/BTU 10 ⁶
Natural gas (g)	0.83	40	48.2	61	1.5	4.4 \$/BTU 10 ⁶ ***
CL(CL/NG price ratio 0.80)**	1250*	24.4	19.5	100	1.3	72 (€/t)

*Specific density square briquette. Bulk density s.b.= 800 ca. (kg/m³)

**NG is necessary for CL cost analysis

***Net of taxes and of dispatching costs. Market price dec. 2013

Therefore the remaining option is to investigate power production at the pre-hydrolysis plant. By constraining the plant to be in a grid supply chain, the transport of cellulignin can be eliminated by

producing power directly with a gas turbine system. For example, if a very large 540 BDT/d plant would produce a net power of 22 MWe after removing the 2.2 MWe parasitic powers required to operate the plant (a conservative vision count 8-10 MWe/wet t). Alternatively, the CL can be shipped with a larger facility but this alternative is more difficult to implement. Although the power option is attractive, it remains that it is another step in the process and the selling of briquettes. Should it be economically feasible it would allow the development of this technology to be implemented in BC to help resolve the bug wood issue. By using the CL to produce power at the pre-hydrolysis plant, this approach decouples the CL from the market price for this commodity and from the requirement for finding a consistent price for this new material. Furfural is still shipped internationally, as the shipping cost is a much lower portion of the overall production cost.

Figure 2 compares the CL energy cost at 0.8 NG price ratio with the oil energy cost. The net cost (production cost) has been calculated taking the value of 6.088 GJ/barrel of TEP and the hypothesis presented in Table 2 (1.3 c€/kWh at 72 €/t of CL). The circle point seems to evidence a strong competition with fossil fuel energy. Other cost components however have to be discussed for the set up of economic evaluation.

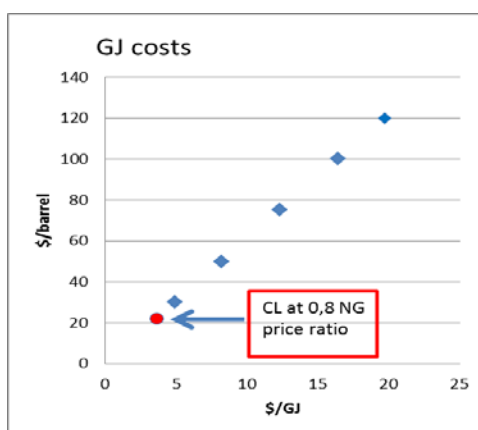


Figure 2. GJ costs at different oil barrel price and comparison with cellulignin energy net cost (Natali, 2008)

5. Pre-hydrolysis as a base step for chemicals

The BEM process may be performed to give electrical and thermal energy through the cellulignin combustion. On the other side the hydrolysate liquor may constitute the platform for chemicals processes. One of the most reliable scheme implementation could be the partial oxidation of cellulignin to CO and H₂. The H₂ from syngas could be utilized to make other fuels by catalytic reduction of alcohols increasing the energy density of molecule by the elimination of oxygen: As example we refer to the 5-hydroxymethylfurfural (HMF) catalytic reaction with hydrogen to yield the potential fuel 2,5-dimethylfuran (DMF) (Romań-Leshkov, 2007). Other chemicals processes may be designed to produce organic specialties.

6. Conclusion remarks

The BEM process produces a powdered solid fuel composed of cellulose (in minor part) and lignin and has very similar physical and chemicals characteristic whatever is the biomass source: bug wood or farmed industry waste or the organic part of urban waste garbage, either dry or wet. The economic return of cellulignin is taken with a pragmatic approach, where it would at first be sold as a fuel replacement for natural gas. Although numerous applications are available, it remains that a long term stable guaranteed market for CL based on natural gas substitution is appropriate, although it may not be the most economic or best long term strategy. As before examined, although natural gas is very convenient to use when available on the spot, there are numerous factors that can decide on the market price for CL substitution. For example, companies wanting to decrease their natural gas cost for heating purposes and areas that do not have access to natural gas will have different price points for switching to cellulignin fuel. Further consideration derives from HHV values and Italian contributes to green energies (CO₂ reduction act). A net

entry can be calculated of 260,000 €/y about (1 batch 30 t/d) to 800,000 €/y (3 batch/d) using conservative parameters¹.

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References

- Natali M., LM Thesis, AA 2009, Technologies for the biomass to energy conversion in Italy: evaluation of a bio-refinery plant.(It). C, Cattaneo University, LIUC, Castellanza, Italy (VA)
- Pinatti D. G., and Soares A. G., 1999 (priority date), Apparatus and Process for a Pre-Hydrolysis of Biomass, US Patent 6,878,212.
- Pinatti D.G., Conte R.A., Borlini M.C., dos Santos B. C., Marcondes M.A., de Oliveira I., Oliveira Montanha R.C., Soares A. G., Romão E.L., Ferreira J. C., Gonçalves Pereira M.L., 2003, Large Scale Low Cost Production of Submicrometric Powder Through Biomass Refinery, *Material Research*, 6, (3), 375-388.
- Pinatti D. G., 2005, Private communications.
- Pinatti D.G., 1999, Proceedings of the Third Meeting of IEA, Bioenergy, Task 17, in Auburn, Alabama, USA., September 6-9.
- Roman-Leshkov Y.J., Barrett C, Liu Zhen Y., Dumesic J.A., 2007, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates, *Nature*, 447, 982-986.
- Tampier M., Beauchemin P.A., Smith D., Bibeau E., 2006, Identifying environmentally preferable uses for biomass resources: BC bugwood: Economics, technical feasibility and GHG implications of seven small to medium-scale technologies. Envirochem Services Inc. for BC Ministry Forests and Range and BC Energy, Mines and Petroleum Resources, Vancouver, B.C. 112 pp. Retrieved March 10, 2008. [<http://www.for.gov.bc.ca/hfd/library/documents/bib97175.pdf>]
- Yasin A., 2008, Study on low environmental impact technologies for waste treatment and re-utilisation. Analysis of the B.E.M. project (Biomass, Energy, Material) proposed for the Brazilian Biomass Program, PhD Thesis, Politecnico di Milano, Italy. PhD Thesis, Politecnico di Milano, Italy.

¹ 2 kg of cellulignin = 1 Nm³ di NG on the HHV base (20 MJ/kg and 37.4 MJ/kg for cellulignin and NG respectively).
 1 batch of cellulignin (30 t) = 15.000 Nm³/batch di NG. Using a conservative ratio of 2 with 7.500 Nm³/batch has a value of 600 Euro/batch (NG cost 0.08 euro/Nm³). Considering 1 batch/day for 320 d/year we have 240000 euro/y. 30000 kWhe/day (1 solo batch; 1 Nm³ di NG = 4 kWhe, 45% efficiency).
 Considering the CO₂, (1 kWh = 450 g di CO₂) 1 year is 4320 t circa di CO₂. The quantity may be substituted by cellulignin. The green rights (6.18 Euro/t CO₂) are 26700 euro/y. So the net entrance is 240000 + 26700 = 266700 euro/y.