POTENTIAL FOR PRODUCTION AND MARKETING OF BIO-OIL BASED CHEMICALS IN CHILE

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Abstract: Chile is poor in fossil fuel resources and therefore strongly depends on imports of crude oil and natural gas with natural gas being mainly imported from Argentina. The use of biomass as fuel or chemical feedstock could help to reduce this import dependency and create value in Chile. Especially by-products of the wood industry represent a major source for potential further use. In the VIII region Bíobío alone, about 790,000 tons of sawdust are produced annually by the wood industry. A considerable part of it is not used adequately since the transport of wood dust over longer distances is economically unviable. An emerging option is the pyrolysis of saw dust to produce bio-oil.

The paper first analyzes the conversion of sawdust to bio-oil via fast pyrolysis techno-economically with the aim to determine bio-oil production costs for Chile. In the second part, options for using the bio-oil are assessed, especially utilizations for contained components and their market potential in Chile. While the sole utilization of bio-oil as a fuel does not seem economically viable, the use of its components as feedstock is seen as an interesting alternative. Potential utilizations meriting more detailed research are proposed.

INTRODUCTION

Chile is a country rich in some mineral but poor in fossil fuel resources. In 2007, 99 % of crude oil and 72 % of natural gas were imported (CNE 2007). Around 80% of the natural gas is imported from Argentina. Hence, temporal shortages or interruptions of Argentinean natural gas exports have severe impacts on Chile's strongly growing economy. In particular during peak demand in winter natural gas supply from Argentina does not meet demand and natural gas fired power plants in Chile have to switch to more costly fuel oil. The substitution of crude oil and natural gas is therefore a prevailing topic of research in Chile.

Chile is with a population of only 17 million one of the major producers of wood products (FAO 2005). The valorization of by-products of the wood industry is therefore not only from an economic point of view interesting but can also contribute to reduce Chile's energy import dependency. Combustion of the wood by-products to produce heat and power is straightforward. However, Chile's ribbon-like shape in combination with a population and forest industry which are unevenly and differently distributed over the country lead to long transport distances for either electricity or by-products rendering direct combustion in many cases less attractive. This explains why a part of the by-products is currently not used adequately and why there is a search for other use options.

One currently discussed option is the upgrading of the by-products to bio-oil using thermo-chemical processes like fast pyrolysis. Bio-oil can be either directly combusted or used for fine chemicals production. Sawdust is suited for this conversion process; it is accruing in large quantities in sawmills where around 17 wt. % of the wood is lost as sawdust. This translates to an estimated sawdust amount of 790,000 t/a for the Chilean region VIII, Bíobío (Walberg 2005). Traditionally, this sawdust is burnt on-site. In larger plants the thermal energy is used to produce process steam or to generate electricity.

The remainder of the chapter is structured as follows. First, some general information concerning wood by-products and their use is given. Then, a techno-economic analysis of bio-oil production by fast pyrolysis including the corresponding material and energy balances are presented. This step is followed by an assessment of the different use options for the produced bio-oil with a focus on its use as a feedstock for fine chemicals production. For this purpose, market potentials of chemicals contained in the bio-oil are regarded.

OPTIONS FOR USE OF WOOD BY-PRODUCTS IN A CHILEAN CONTEXT

Chilean wood industry is characterized by both natural forests and plantations of fast growing species like eucalyptus and pine trees. The wood industry is concentrated in the Chilean regions VII to X with large plants dominating the production. This localization has a strong impact on the use options for forestry by-products as the supply is limited to a few regions and concentrated in a rather limited number of places.

Direct combustion for heat and/or power production is a straightforward option to use the by-products but the concentration of the supply in a few regions and places makes it necessary to transport either the by-products or the produced power. In case of sawdust its use in existing combustion plants may induce high costs for retrofitting and its low volumetric heating value makes a transport economically and energetically unattractive. One possible solution for improving sawdust utilization is its processing with the aim to increase the heating value and to improve its handling and usability in existing installations. For processing the larger amounts of sawdust accruing at certain wood processing sites are even favorable as economies of scale can be realized.

In the following, the fast pyrolysis of sawdust to bio-oil is techno-economically analyzed. Bio-oil is a brown acidic liquid with a smoky smell and contains 20-40% water with effects on its chemical and physical stability (A.V. Bridgwater and Grassi 1991). Bio-oil is nevertheless to some extent comparable to crude oil. It is not only usable as a combustible in especially adapted engines but also as a feedstock as it contains valuable chemical compounds resp. groups of chemical compounds.

BIO-OIL PRODUCTION BY FAST PYROLYSIS

Principles of fast pyrolysis

Fast pyrolysis, principally a thermal degradation, is a thermo-chemical process that converts finely ground biomass by rapid heating to 350-800°C under the absence of oxygen to bio-oil, gas and char. Their proportions depend on the process conditions and the feedstock. Bio-oil yield is highest in a fast or flash pyrolysis which is characterized by extremely high heating rates, short residence times and rapid product quenching (A.V. Bridgwater and Grassi 1991). Fast pyrolysis has been a subject of research for at least 50 years and a variety of pyrolysis reactors were designed with the fluidized bed reactor being the most advanced and promising one. However, only small-scale or demonstration plants are in operation.

Basically, two fluidized bed reactor types can be distinguished: The first is the circulating or entrained bed reactor type, which uses a heat carrier that is entrained by a gas in a loop through the reactor. This reactor type is used already on a larger scale, e.g. in refineries. Due to high friction between the heat carrier particles and the piping energy, costs are high and feedstock particles have to be ground to 1-2 mm (Ringer, Putsche, and Scahill 2006). The second one is the fluidic or bubbling bed reactor type for which ample experience exists in the chemical and refinery industry (Ringer et al. 2006). Feedstock for this type of reactor is ground to a particle size of 2-3 mm. The feedstock passes through a heat carrier bed.

As a pyrolysis plant consists not only of the reactor but also of units for heating, quenching, storage and piping it is assumed that the investments for both reactor types are comparable (Stewart 2004). Furthermore, several studies have shown that energy consumption and production costs do not differ considerably between a fluidic bed and circulating bed reactor either.

Materials and energy balance

A materials and energy balance was calculated for the bio-oil production plant based on published data which originate mainly from the Canadian Company Ensyn Technologies Inc. The process was modeled using the Petri Net based LCA-software tool Umberto®. Figure 1 shows a snapshot of the main process steps (reactor, cyclone, quenching and auxiliaries) and associated material and energy flows. Each of the process steps was modeled in more detail in a sub-model.

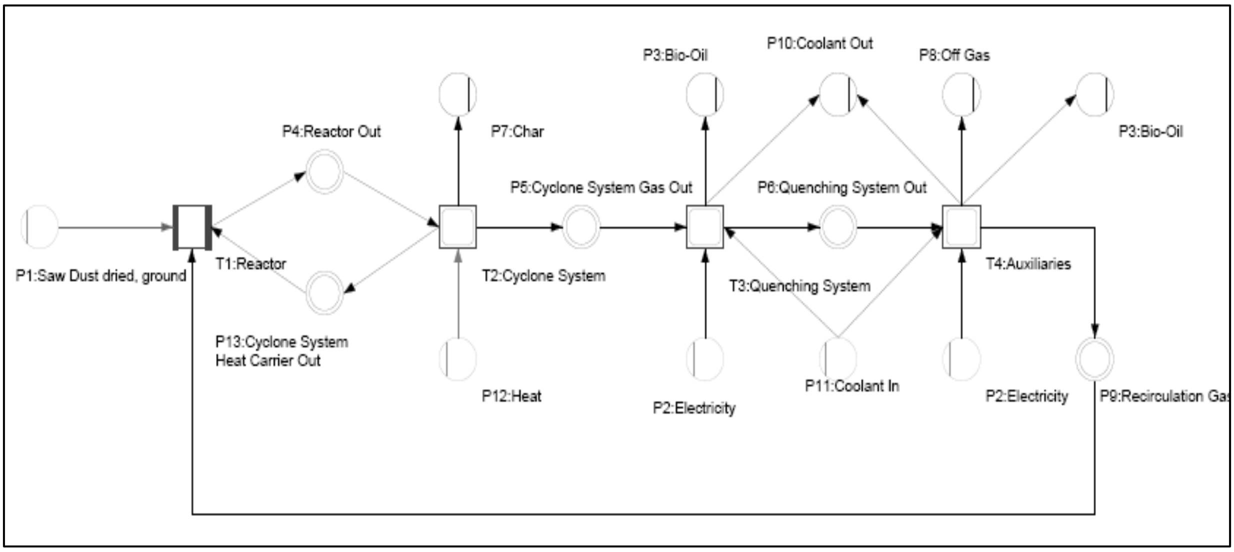

FIGURE 1: Main process steps of bio-oil production plant as a Petri Net in the software tool Umberto®

A summary materials and energy balance for the production of bio-oil in Chile is given in Table 1. The estimated bio-oil yield is 77.5%. Besides bio-oil, considerable amounts of non-condensable gases and char are produced. For producing the required process heat, about 70 kg of the produced char have to be burnt. Burning the non-condensable gases alone would provide about 80 % of the required heat. Assuming an efficiency of at least 15 % for electric power generation, non-condensable gases and char contain more energy than necessary to produce both, the necessary process heat and electric power.

TABLE 1: Summary of materials and energy balance for bio-oil production

1000 kg of sawdust yields	Processing of 1000 kg of sawdust demands
• 6 kg of ash • 108 kg of char • 110 kg of non-condensable gas • 775 kg of bio-oil	• 53 MJ (15 MWh) of electric energy • 1,600 MJ (445 MWh) of heat

Bio-oil production costs

The production costs of bio-oil are the sum of investment related costs (depreciation, imputed interests, maintenance and repair, assurance etc.) for the different parts of the plant, in particular the parts for the preprocessing of the feedstock and the pyrolysis, and operating costs (wages, energy costs, raw materials costs, consumables etc.).

For the **estimation of investment** of the plant an underlying production capacity of 75,000 t/year of bio-oil is assumed. Assuming a yield of 75% of bio-oil in case of sawdust, this equals a feedstock capacity of 100,000 t/year of sawdust (dry) and a catchment area of about 50 km around the plant. The investment for this plant including a highly-efficient fabric filter was estimated to be US$28 million (2005) based on a literature review (cf. A. V. Bridgwater and Peacocke 2000; McKeough 2005; Mullaney 2002; Östman 1999; Ringer et al. 2006; N.N. 2004) and data of a planned pellet plant in Chile. Main investment items are the pyrolysis module with US$17 million and the preprocessing module with US$9 million.

For the calculation of the bio-oil **production costs**, an interest rate of 8% and a service life of 10 years were assumed leading to an annuity factor of 15%. Annual maintenance and overhead costs were calculated as 2.5% and 2% of the investment sum respectively. Although the forestry sector is a well-established industry in Chile, prices for sawdust are relatively low with only US$19 per ton compared to US$70 per ton in Europe (Brammer, A. Bridgwater, and Lauer 2005), leading to annual feedstock costs of US$1.9 million per year. Electricity costs for both the feedstock and the pyrolysis module sum up to US$0.8 million per year. Costs for vehicles operation and labor are US$0.2 million per year each. Annual operational costs sum up to US$3.1 million per year leading to total costs of US$8.4 million per year or US$123 per ton of bio-oil produced.

The highest uncertainty exists concerning the investment for the pyrolysis unit with a high probability that learning effects on the technical side and sales volume on the market side could in future lower the price considerably. A sensitivity analysis shows that if the investment sum is reduced by 30%, production costs would be reduced by 14%. A reduction of the same percentage of the investment sum of the pyrolysis module would reduce production costs by only 9%. The reduction of feedstock and electricity costs by 30% could lower production costs by 10 % and 6 % respectively. Labor costs are only contributing with 1.5% and thus have only a minor influence on production costs.

USE OF BIO-OIL AS A FUEL

Bio-oil has a density of around 1.2 kg/l and a lower heating value of 18 MJ/kg which is less than half of that of fuel oil, but which still results in significantly lower transport costs compared with sawdust (Soltes and Milne 1988). The exact heating value and composition of the bio-oil depends on the feedstock utilized for fast pyrolysis. Bio-oil is more suitable for storage and is pumpable. As it is derived from biomass it can be burnt nearly CO_2-neutral. One disadvantage of bio-oil is the non-solubility without additives with common fuel oils and organic solvents. It is therefore not possible to use the existing fossil fuel distribution system for the distribution of bio-oil (A.V. Bridgwater and Grassi 1991). Besides, it is not as stable as diesel fuel and changes its composition over time. However, kept under 25°C and without contact to air bio-oil can be stored for up to two years. Other unfavorable properties are its water content which can be as high as 30%, its high kinematic viscosity of approximately 112 cSt at 20 °C and its strong acidity. Finally, it is less homogeneous than other fuels so that specially modified burners or engines have to be used.

If bio-oil is used in a boiler or engine, it must compete with other combustibles available in Chile like fuel oil No. 6. As the lower heating value of bio-oil is around 53% of that of fuel oil, the target price of bio-oil must be lower than the fuel oil price by at least the same percentage, i.e. cheaper than US$196 per ton at the time of the study (2007; Fuel Oil No. 6 price was US$370 per ton) (please note that prices for fossil fuels vary considerably over time and have decreased considerably afterwards).

USE OF BIO-OIL AS A FEEDSTOCK

Bio-oil contains a large number of chemical compounds. Estimates range from about 100 to 400 compounds (Diebold 2002). The main components of bio-oil are given in table 2. The chemical composition can drastically change from one feedstock to another or as a result of process modifications. Predictions of the shares of individual compounds are even more uncertain.

TABLE 2: Representative chemical composition of fast pyrolysis derived bio-oil (Bridgewater, Czernik, and Piskorz 2002)

Chemical compound	Mass %
Water	20-30
Lignin fragments: insoluble pyrolytic lignin	15-30
Aldehydes, e.g. formaldehyde, hydroxyacetaldehyde	10-20
Carboxylic acids, e.g. acetic acid, propionic acid	10-15
Carbohydrates: e.g. glucose, levoglucosan	5-10
Phenols, e.g. phenol, 3,5-dimethylphenol	2-5
Furans and furfurals	1-4
Alcohols, e.g. methanol, ethanol	2-5
Ketones, e.g. acetone, MEK	1-5

Screening of chemical compounds in bio-oil for use as feedstock

Overall there is only little information available about the shares, possible uses and economic values of the different compounds in bio-oil highlighting the need for a further analysis. Potential utilization of single chemicals, chemical groups/fractions contained in the bio-oil as well as of the whole bio-oil and of charcoal were analyzed. Overall more than 180 chemicals have been screened for their potential utilizations by their chemical abstract service (CAS) registry number. To make the different compounds and their utilizations comparable against each other an indicator framework was developed with indicators for quantity in bio-oil, price, market size, patent maturity and market applicability leading to a ranking. Table 3 shows the three best-ranked compounds respectively utilizations for the four groups: chemicals, chemical groups/fractions of the bio-oil, whole bio-oil and charcoal. A major obstacle for assessing the market potential of the compounds is that so far only two chemicals, hydroxyacetaldehyde (HAA) as a browning agent and liquid smoke as food aroma, were successfully introduced to the market. Concerning other utilizations there is only limited information available regarding their commercial viability. However, costs for separating the chemicals from the bio-oil were not analyzed in detail.

Most promising chemical compounds in bio-oil for use as feedstock

The three highest ranked compounds respectively utilizations in the indicator framework were reassessed to identify the most promising chemicals and utilizations for Chile for which a more detailed market analysis for Chile was considered fruitful.

Chemicals: Levoglucosan was selected as promising (marked by the bold letters in table 3) because of its wide range of possible utilizations and because of its abundance in the bio-oil. HAA has been analyzed to be the single most abundant chemical contained in the bio-oil and has been identified as a potential chemical for high value added applications, e.g. as a browning agent. It seems promising therefore, to look for possible market opportunities for these products in Chile. Acetol on the other hand, did not convince in terms of end-product applications.

Chemical groups/fractions: Even though there is a wide utilization area for liquid smoke in the Chilean salmon industry it was considered as not promising as liquid smoke is patented. However, the phenolic rich phase seems promising as it can be used as a phenol substitute in phenol-formaldehyde (PF) resins for the Chilean fiberboard industry. Carboxylic acids are also considered as promising due to their high market prices and their possible utilization as a silage additive.

TABLE 3: Indicator-based ranking of usages for bio-oil and components (substances in bold letters are those for which a market analysis for Chile was considered promising)

Rank	Chemicals	Groups/Fractions	Whole bio-oil	Charcoal
1	**Levoglucosan**	Liquid smoke	Preservative (for creosote replacement)	Sequestration
2	**Hydroxyacetaldehyde (HAA)**	**Phenolic rich phase**	Slow release fertilizers	Fertilizers
3	Acetol	**Carboxylic Acids**	BioLime & NOx control	Activated carbon

Market analysis for selected chemicals and chemical groups/fractions in Chile

Phenolic rich phase: The phenolic rich phase can be used as a phenol substitute in phenol-formaldehyde (PF) resins with the main market application as a glue binder in man-made wood products (Graham, 2003). PF resins are mainly used in the production of oriented strand board (OSB), plywood and wafer boards where they represent 2.5 to 10.0 wt% of the dry material. The total industrial consumption of PF resins in Chile is estimated to be 62,500 tons in 2007. The phenolic rich fraction can replace up to 40 wt% of the phenol in PF resins. Imports of phenolic resins to Chile amounted to 4.300 tons in 2007 representing a market value of US$4.2 million. As the phenolic rich phase is used as a technologically proven phenol substitute the extraction of a phenolic rich phase is highly interesting.

HAA: HAA can be used as a raw material for the production of glycolic acid. The production of glycolic acid from HAA would require special treatment though, and a rising demand on glycolic acid is not expected in the near future. HAA seems therefore unfavorable if the focus is on current markets in Chile.

Carboxylic acids: Carboxylic acids get high prices and are used as a chemical silage additive. The demand for chemical silage additives in Chile is high and has so far not been satisfied. Approximately one million tons of silage is lost in Chile every year because of a lack of required chemical silage additives. The demand for a reasonable priced silage additive in Chile is therefore expected to be very high. The carboxylic acids have been evaluated as a potential silage additive by (Jahn 2008) but it is still unclear how much of the carboxylic acid rich phase has to be used to successfully improve the silage quality. The chemical silage additives are thereby mainly used on high-risk silage with a dry mass percentage of less than 30% as under these conditions the formation of natural carboxylic acid is not sufficient to lower the pH value to the required value of about 3 to 4 (Fillipi 2007). Furthermore, when silage is covered with oxygen impermeable folia, the uppermost layer directly below the folia will not be completely free of oxygen. As this layer represents a significant part of the whole silage, losses of 20 wt% occur (Jahn 2008) which could be reduced or even avoided if carboxylic acids were added.

CONCLUSIONS

In Chile by-products of the forestry industry like saw-dust arise in large quantities in regions VII to X. As there is a strong interest in Chile to reduce dependency from fossil fuel imports and to generate added value in the country, innovative options for use of the sawdust like its fast pyrolysis to bio-oil is currently discussed. Bio-oil may replace fuel oil as combustible but can be also used as a feedstock. Chile does not provide major subsidies for green technology (Binkert 2005). Thus, if used as combustible, it competes directly with fuel oil. Our analyses show that high investments for the pyrolysis plant and hence production costs for bio-oil represent an obstacle for competitiveness as a combustible.

However, the use as a feedstock could be economically attractive as certain chemicals in the bio-oil can be used for high valuable applications in a Chilean context. Liquid smoke and HAA are examples for products being already on the market which could be extracted from the bio-oil. Intellectual property rights and a limited market make their production, however, less attractive in a Chilean context. Extraction of a phenolic rich phase and its use to replace phenol in PF resins as well as of carboxylic acids and their use as silage additive are considered as highly interesting. These options which could contribute to make the production of bio-oil economically viable in Chile need further analyses.

Considering a future perspective with most probably rising crude oil prices, continued research on the production of bio-oil in Chile and its use both as a combustible/fuel and as a source of valuable chemical products seems highly advisable.

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REFERENCES

Binkert, U. 2005. *Chiles Energiewirtschaft sucht Wege weg vom Gas*. Santiago de Chile: Bundesagentur für Außenwirtschaft.

Brammer, J., A. Bridgwater, and M. Lauer. 2005. "Opportunities for Bio-Oil in European Heat and Power Markets." pp. 179-206 in *Fast Pyrolysis of Biomass: A Handbook Volume 3*. Chippenham: CPL Press.

Bridgewater, A., S. Czernik, and J. Piskorz. 2002. "The Status of Biomass Fast Pyrolysis." pp. 1-22 in *Fast Pyrolysis of Biomass: A Handbook Volume 2*. Chippenham: CPL Press.

Bridgwater, A. V., and G. V. C. Peacocke. 2000. "Fast pyrolysis processes for biomass." *Renewable and Sustainable Energy Reviews* 4:1-73.

Bridgwater, A.V., and G. Grassi. 1991. *Biomass Pyrolysis Liquids Upgrading and Utilisation*. New York: Elsevier Science & Technology.

CNE. 2007. "CNE - Comisión Nacional de Energía." http://www.cne.cl/cnewww/opencms/06_Estadisticas/Balances_Energ.html (Accessed September 3, 2009).

Diebold, J.P. 2002. "A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils." pp. 243-292 in *Fast Pyrolysis of Biomass: A Handbook* Volume 2. Chippenham: CPL Press.

FAO. 2005. "Forest products yearbook 1999-2003 / Produits forestiers annuaire 1999-2003 / Productos forestales anuario 1999-2003 /." http://www.fao.org/docrep/008/y5985m/y5985m00.HTM (Accessed September 3, 2009).

Fillipi, R. 2007. "Conceptos Básicos en la Elaboración de Ensilajes." www.lacteos.watts.cl/images/Img_Editor/DocAdjuntos/Conceptos%20Bsicos%20en%20la%20elvoracin%20de%20ensilajes,%20Osorno%2020%20Nov%2007.pdf, accessed 10.12.2007.

Jahn, E. 2008. *Fast Pyrolysis Derived Carboxylic Acids as Silage Additives*. Chillan (Chile): Instituto de Investigaciones Agropecuarias.

McKeough, Paterson. 2005. *Techno-economic analysis of biotrade chains : upgraded biofuels from Russia and Canada to the Netherlands*. Espoo: VTT.

Mullaney, H. 2002. *Environmental and Economic Feasibility of Bio-Oil in New Hampshire'sCountry*. New Hampshire Industrial Research Center (NHIRC) http://www.unh.edu/p2/biooil/bounhif.pdf.

N.N. 2004. *New Hampshire Bio-oil Opportunity Analysis*. Concord, NH: Innovative Natural Resource Solutions LLC http://www.inrsllc.com/download/NH_bio_oil_analysis.pdf.

Östman, A. 1999. *Comparison of alternative routes for biomass fuel: biomass (pellets), pyrolysis oil and tall oil pitch*. Sweden: Keminformation, AB.

Ringer, M., V. Putsche, and J. Scahill. 2006. *Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis*. National Renewable Energy Laboratory http://www.nrel.gov/docs/fy07osti/37779.pdf.

Soltes, Ed, and T. Milne. 1988. *Pyrolysis oils from biomass : producing, analyzing, and upgrading*. Washington DC: American Chemical Society.

Stewart, G. W. 2004. *Bio-Oil Commercialization Plan*. Cole Hill Associates for the NH Office of Energy and Planning http://www.bioenergypartners.com/NH-bio-oilcommercializationplan.pdf (Accessed September 3, 2009).

Walberg, F. 2005. *Disponibilidad de Madera Residual en Chile*. Unpublished technical report: Unidad de Desarollo Tecnológico, Universidad de Concepción.