Kouhia, Mikko; Holmberg, Henrik; Ahtila, Pekka

**Microalgae-utilizing biorefinery concept for pulp and paper industry: Converting secondary streams into value-added products**

*Published in:*
ALGAL RESEARCH

*DOI:*
10.1016/j.algal.2015.04.001

Published: 01/01/2015

**Document Version**
Peer reviewed version

*Please cite the original version:*
Microalgae-utilizing biorefinery concept for pulp and paper industry: converting secondary streams into value-added products

Mikko Kouhia, Henrik Holmberg, Pekka Ahtila

Abstract

Traditional pulp and paper industry is in transition due to increased competition and changes in consumption habits. Advanced biorefining is seen as one option to create new business opportunities. This article presents a microalgae-utilizing biorefinery which is integrated into a traditional pulp and paper mill and which produces high-value algal products, fertilizer and biogas from secondary process streams. Presented biorefinery process is validated with mass balances, employing initial data from a Scandinavian pulp and paper mill. Results indicate that the proposed process is technically viable. Production potential is sensitive to light and nutrient availability in algae cultivation, and seasonal changes in irradiance result in significant output variation. The biorefinery process can be generalized to other process industry and wastewater treatment plants that have similar output flows.

Keywords: biogas, biorefinery, fertilizer, mass balance, microalgae, process integration

1. Introduction

The need to reduce waste generation and to recycle waste streams more effectively has arisen globally, driven by motivators such as increasing environmental awareness, growing population and depleting natural resources. Regulations as well as material and waste handling costs direct the pressure towards industry to utilize their material streams as effectively as possible. Substituting virgin feedstock consumption with secondary material or energy flows — potentially usable by-products from another process — can contribute to the reduction of the total impact on the environment.

Process integration is an approach where separate industrial processes are combined to create additional value [1]. Integration enables streams, which would otherwise be disposed of due to lack of economic feasibility or no possibilities of further usage, to be used as an input for another process. Consequently, raw material consumption, waste generation and primary energy consumption may be reduced.

Competitive position in the pulp and paper industry has changed rapidly during the last decade. Graphic paper production is in dire straits, while global demand for pulp, paperboard and specialty products is increasing. Main drivers for the structural change include decreasing product prices, increasing wood costs, increased competition from low-cost producers, increased energy prices and declining newsprint usage [2 3]. Therefore companies are forced to search for new value-creating business opportunities [4]. Producing additional high value products with advanced biorefineries is one strategic option that could allow regaining competitive advantage.

Biorefining is defined as “the sustainable processing of biomass into a spectrum of marketable products and energy” [5]. Even though biorefineries are characterized by the variety of products, the current main driver is the demand for renewable fuels, initiated by environmental policies [6]. Recent forest industry biorefinery studies have focused mostly on black liquor and biomass gasification, and hemicellulose extraction [see e.g. 7 8 9]. In most studies, fuels are the main product, but also value-added products such as hydroxy acids and xylans have been investigated [e.g. 10 11].

Most biorefinery concepts for forest industry focus on lignocellulosic material flows, but biorefining could also be based on other material streams: one possible option is utilizing secondary streams for microalgae cultivation. Microalgal biomass production offers several advantages: for instance, microalgae are easy to cultivate, have high growth rates in comparison to conventional forestry or agricultural crops, require little land area and can consume water that is unsuitable for human consumption [12]. The range of products from microalgae is wide, including biofuels and high-value products such as polyunsaturated fatty acids (PUFAs), pigments and proteins [13].

One major drawback for microalgae is their high production cost, particularly in harvesting and dewatering steps, and for instance utilization of microalgae-based biofuels has been impeded by these processing costs [14]. Cultivating microalgae for producing a single energy carrier has not yet proven to be economically feasible [15 16].
but implementation of carbon dioxide sequestration from flue gases, treating wastewaters, producing another energy product and/or co-producing higher value products are considered to positively contribute to economical feasibility [12, 17, 18, 19].

Ashes and sludges comprise a waste problem in a pulp and paper mill. Both biomass ash and anaerobic digestion residue contain nutrients that can be recycled; therefore their application as fertilizer has been studied recently, as well as combining ashes and undigested sludges to produce fertilizer [see e.g. 20, 21, 22]. Calculated savings in combined ash–sludge fertilizer production have been calculated to be significant in comparison to landfilled [23].

Available raw materials and secondary heat flows at a pulp and paper mill enable algae cultivation as well as methane and fertilizer production. Some algae-utilizing biorefinery concepts have been presented previously, where algae are grown in anaerobic digestion effluents [see e.g. 21, 25, 26, 27], algae matter is digested [17, 20, 23, 26, 18], algal matter is digested [17, 20, 23, 26, 18], nitrogen and phosphorus are returned to digestion. The biorefinery is designed to produce as many valuable products as possible and to utilize secondary streams that otherwise would have to be disposed of. The most desired products are algal lipids, then biofertilizers and finally fertilizers [24, 25, 26, 28, 29, 30, 13], but a process that integrates all of these has not yet been presented.

This article presents a microalgae-utilizing biorefinery concept, which would be integrated into a traditional pulp and paper mill to convert secondary streams into value-added products. Product flows and mass balances are simulated, employing input data from a Scandinavian pulp and paper mill. The effect of seasonal variation and the location of the biorefinery is considered and the sensitivity to input parameter variation is examined.

2. Materials and methods

2.1. Biorefinery concept

A schematic diagram of the proposed biorefinery process is presented in Figure 1. This BioA process [see patent: 31] consumes flue gases, nutrient rich sludge and ash to produce ω-3 fatty acid containing lipids, methane and fertilizer. The outlined process is also suitable for producing other algal extracts. In the proposed scheme, mill wastewaters are treated in an existing biological wastewater treatment plant, in which activated sludge process follows primary sedimentation. The wastewater treatment plant produces waste activated sludge (WAS), consisting of microbial matter and residue from the wastewaters.

In digestion a part of WAS is converted into methane and some of the nutrients in incoming matter are released into soluble form. Biogas that is released in digestion is collected and upgraded. The digested residue is pumped to hygienization and then to mechanical dewatering, where the water content is reduced and the dewatered stream is directed to fertilizer production via thermal drying. Fly ash from pulp and paper mill boilers is separated into fine and coarse fractions, and the heavy-metal-rich fine fraction is removed as reject. Accept from ash classification is mixed with the digested solids in order to produce fertilizer.

In the proposed process, liquid effluent from the mechanical dewatering of digested residue is utilized as algal growth medium. The algae consume nitrogen and phosphorus in the effluent, and carbon dioxide in flue gases that originate from biomass boilers at the mill. As the algae grow, they produce oxygen, which is removed from the reactors alongside with the unused flue gas components. Algal mass is continuously removed from cultivation and excess water is concurrently removed from the stream. Some water is recycled back to the growth cycle to dilute the digestion effluent stream and to keep the amount of water in cultivation constant; the rest is conveyed to the wastewater treatment plant. Alternatively, dilution water to cultivation can be provided from treated wastewaters. Nutrient content in the algal growth medium at cultivation exit should be at such a low level that it can be disposed of without the risk of eutrophication. After dewatering, lipids are extracted from algae, and the remaining components are returned to digestion.

The biorefinery is designed to produce as many valuable products as possible and to utilize secondary streams that otherwise would have to be disposed of. The most desired products are algal lipids, then biofertilizers and finally biogas or biomethane. In addition, oxygen and ash reject are produced, of which the former can for example be consumed in bleaching or combustion processes at the pulp

---

Figure 1: Evaluated biorefinery configuration: waste activated sludge (WAS), ash and flue gas from a pulp and paper mill are consumed in lipid, methane and fertilizer production whilst utilizing algae in the conversion process.
and paper mill, and the latter as an additive in concrete production. It is anticipated that the digestion effluent provides a good substrate for the algae and little or no additional nutrients are required. Photobioreactors are chosen instead of other algae cultivation methods in order to prevent contamination, to increase controllability and to enable capture of produced oxygen. Excess heat from the pulp and paper mill can be exploited in photobioreactor, digestion, hygienization and other equipment that requires heat input.

2.2. Calculation principles

Technical feasibility of the process is demonstrated with a case study: mass balances are solved in order to show process outcome and to have a basis for later studies. Maximum product yields and annual variation are calculated using initial assumptions and the effect of plant location is evaluated by altering lighting conditions. Further feasibility assessment is not yet conducted at this stage — economic assumptions used in the calculations. Data from a Scandinavian pulp and paper mill is employed, alongside with literature data. Realistic process values that are achievable with current technologies are chosen; *Nannochloropsis* algae are selected based on preliminary cultivation tests.

Biogas productivity in WAS digestion is computed based on volumetric methane production potential per added volatile solids (VS) and WAS mass flow. As algae digestion output may vary largely depending on the composition, gas output is estimated with theoretical reaction equation, where 50% of carbohydrate, lipid and protein in algal matter are assumed to be reacted according to [41]

\[
\text{C}_n\text{H}_b\text{O}_a\text{N}_c + \left( n - \frac{a}{4} \right) \frac{b}{2} + \left( \frac{3c}{8} \right) \text{H}_2\text{O} \\
\rightarrow \left( \frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right) \text{CH}_4 + \left( \frac{n}{2} - \frac{a}{8} \right) \frac{b}{4} + \left( \frac{3c}{8} \right) \text{CO}_2 \\
+ c\text{NH}_3. \tag{1}
\]

Coefficients a, b, c and n are obtained from elemental analysis of the digested matter. It is presumed that nutrients in the digested matter are distributed after digestion according to VS destruction percentage: nutrients in disintegrated solids will be dissolved and the rest remain in solid phase.

In order to calculate potential algae growth and fertilizer composition, absolute nutrient flows in digestion are analysed. It is assumed that there are no nitrogen or phosphorus losses and that produced ammonia exits the reactor in dissolved form. As some water and dissolved nutrients will go with the solid stream, the effluent and nutrient flows are calculated based on mass balances in dewatering.

It is assumed that algae will consume nutrients in their growth according to their composition; consumption of a specific nutrient can thus be expressed with algal growth rate \( \dot{m}_{\text{algae}} \) and the proportion of element \( i \) to algal dry matter as obtained from elemental analysis: \( m_i = \dot{m}_{\text{algae}} \cdot \frac{\dot{w}_i}{w_i} \), where \( w_i = m_i / \dot{m}_{\text{algae}} \). As the available mass flows of nutrients and carbon are known in this case, maximum growth rate of algae can hence be determined as

\[
\dot{m}_{\text{algae}} = \min_i \left( \frac{m_i}{w_i} \right). \tag{2}
\]

Here it is presumed that algae will grow until first nutrient source is depleted. Nutrients originate from digestion effluent and possible nutrient addition; carbon originates from carbon dioxide in flue gas. Only nitrogen, phosphorus and carbon are used in these calculations in determining the possible growth rate; other elements are not taken.
into account. In steady state operation algal growth rate from Equation 2 equals mass flow rate of biomass that is removed from cultivation.

Algal growth rate is dependent on cultivation system characteristics, but since reactor dimensions are not defined in this study, laboratory-scale growth data from Nannochloropsis cultivation in tubular photobioreactors is employed. It is assumed that achievable volumetric growth rate is linearly dependent on available photosynthetically active radiation (PAR) and it is 0.7 kg m\(^{-3}\) d\(^{-1}\) at 1030 µmol m\(^{-2}\) s\(^{-1}\) average daily radiation on photobioreactor surface [42]. Daily irradiance data for Helsinki, Finland (N 60.2°, E 24.9°) [43] is used for case evaluation and a conversion factor of 4.6 µmol J\(^{-1}\) is utilized in converting total irradiance to number of photosynthetically active photons.

The photobioreactor size is dimensioned in this analysis according to peak volumetric productivity, so that all nutrients are consumed on the brightest day and decreased volumetric productivity restricts algal growth during the rest of the year. Due to mutual shading of photobioreactor tube arrays in a large system, average light intensity on tube surface differs from irradiance on ground level. This is taken into account with suggestive correction factor derived from light intensity measurement in a photobioreactor system [44]; light intensity at photobioreactor surface is assumed to be 0.7 times the incident light intensity. This parameter only affects calculated photobioreactor size.

3. Results and discussion

3.1. Material outputs

Biorefinery mass flows at peak algal productivity are shown in Table 2. To evaluate the importance of algal residue recycling, simulation results are compared to an alternative case where there would be no recycling. Feedback of algal residue into digestion and the consequent nutrient recirculation allows significantly higher algal growth in comparison to the case with no recycling; proposed process enables 15 t d\(^{-1}\) maximum algal growth, which is 42 % higher than without recycling. Similarly, 64 % more methane and 24 % more fertilizer would be produced. CO\(_2\) requirement, oxygen production and lipid production are all linearly dependent on attainable algal growth rate. Greater algal growth, and correspondingly greater digestion residue generation, allows increased fertilizer production when algal residue is recycled. With recycling, algae-bound nitrogen and phosphorus are returned to digestion, and they eventually end up in solid digestion residue and consequently in fertilizer.

Experimental data on algae cultivation, co-digestion and lipid extraction in proposed system are required for more precise analysis. Production sensitivity to most significant parameter variation is displayed in Figure 2 where one input parameter (see Table 1) is modified at a time and changes to outputs are recorded individually. Figure 2 indicates that all simulated product flows are linearly dependent on waste activated sludge (WAS) input. In the presented case, phosphorus content is limiting growth and hence nitrogen addition would not be beneficial. Attainable algae production based on nitrogen and phosphorus availability are however on the same level: available phosphorus in the growth medium restricts growth to 15 t d\(^{-1}\), while 17 t d\(^{-1}\) algae could be produced if all nitrogen could be consumed. Phosphorus addition of 6.5 kg d\(^{-1}\) would allow all nitrogen to be consumed.

Attainable algal growth is determined by the amount of available nutrients. As all nitrogen and phosphorus are assumed to be bound to proteins, lower algal protein content would lead to decreased nutrient requirements, and thus increased growth potential. This can be seen in Figure 2. On the other hand, nutrient availability to algae is affected by the volatile solids destruction in digestion. WAS decomposition has larger effect on algae growth than algae decomposition, because all incoming nutrients are bound to WAS, and only a part of those are released and consumed by the algae.

Sensitivity of methane production resembles algal growth sensitivity. However, parameters which only affect algae production have smaller effect on methane production than those, which also have direct consequences on digestion; in the simulation 30% of produced methane originates from algal residue decomposition. Calculated methane yield in lipid-extracted algal residue digestion would be 160 kg t\(^{-1}\) added volatile solids, which is in the range of published experimental results [e.g. 37]. Fertilizer mass flow is linearly dependent on WAS flow rate, but its sensitivity to other parameter variation is low: the flow is only slightly affected by amount of incoming nutrients to digestion. Nutrient content in fertilizer is determined by corresponding nutrient content in ash and WAS, and to smaller extent algal growth.

In general, any organic waste stream with substantial amount of nutrients may be digested to provide biogas, substrate for algae and a basis for fertilizer. Digestion input material properties fully determine the applicability

| Table 2: Simulated case study outcome at calculated peak algal productivity of 0.61 kg m\(^{-3}\) d\(^{-1}\), indicated on dry mass basis. Results are shown separately for the case with algal residue digestion and corresponding nutrient recycling, and additionally for a case where no recycling takes place. |
|-----------------|-----------------|-----------------|
|                 | Recycling       | No recycling   |
| Algae growth    | t d\(^{-1}\)     | 15              | 10              |
| CO\(_2\) requirement | t d\(^{-1}\)     | 29              | 20              |
| Oxygen production | t d\(^{-1}\)     | 21              | 15              |
| Lipid production | t d\(^{-1}\)     | 3.2             | 2.2             |
| Methane output  | t d\(^{-1}\)     | 4.6             | 2.8             |
| Fertilizer flow rate | t d\(^{-1}\)     | 55              | 44              |
| Fertilizer N content | %               | 2.6             | 2.5             |
| Fertilizer P content | %               | 0.90            | 0.90            |
| Fertilizer K content | %               | 0.60            | 0.60            |
| Photobioreactor volume | 10\(^{3}\) m\(^{3}\) | 24              | 17              |
of the concept, since they directly affect algal growth and biogas production, and also indirectly fertilizer composition. As municipal wastewaters typically contain more nutrients than industrial wastewaters, utilizing those streams should correspondingly result in greater product yield in comparison to the calculated case. Since wastewater properties can largely vary depending on their origin, and the purpose is to produce fertilizers and edible products, it is crucial to investigate case-by-case whether the process can be applied to the specified inputs.

The nutrient content in simulated case study fertilizer is lower but comparable to organic fertilizers that are currently on market [see e.g. 45]. Desired nutrient content in a fertilizer depends on the crop requirements, and the fertilizer value is influenced by the nutrient content. Nutrient content in the biorefinery fertilizer can be adjusted with ash-to-digestion residue ratio as displayed in Figure 3.

If less ash is used, nitrogen content increases, but share of phosphorus and potassium decrease. The nutrient content can also be improved by providing e.g. manure or other nutrient-rich feedstock to digestion or directly to the product. Adding conventional fossil-based fertilizer components is also possible, but insensible if the goal is to produce a renewable fertilizer. Product usability requires to be determined individually for each case — in some cases, heavy metal concentration in ash or sludges may prevent material to be used as fertilizer.

Simulated product output varies remarkably with the seasons, because irradiance changes throughout the year and algae productivity is assumed to be linearly dependent on available light. Calculated production for an average year in Helsinki is plotted in Figure 4, while lipid production is practically nonexistent during the winter, minimum fertilizer and methane production are still 81% and 62% from their respective peak values. Even though fertilizer mass flow varies, its composition remains approximately the same throughout the year, because ash to digestion residue ratio remains at a constant level.

Annual operational data is summarized in Table 3, which also displays the effect of light variation on built capacity utilization: due to variation only 41% of installed cultivation and 77% of digestion capacity can be exploited on average; 89% of all ash that could be consumed with peak performance may be used on annual basis. Only 36% and 1% of total available ash and CO₂ would be utilized in the simulated case. Peak capacity factors can be adjusted with dimensioning: since volumetric growth rate of algae is restricting growth in darker periods, building larger equipment would enable greater growth during those periods.

To overcome the low algal productivity in winter, additional lighting could be provided to cultivation. In addition to an increase in algae growth, artificial lighting would also enhance fertilizer and methane production and thus increase the biorefinery utilization factor. Artificial lighting and reactor size optimization are both subject to financial
Table 3: Annual variation of input and output flows in the case study. Material utilization is defined by the share of used feedstock to all available material from the pulp and paper mill, while peak capacity factor is the share of annual material flow to the amount that could be produced or consumed with equipment peak capacity.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WAS</td>
</tr>
<tr>
<td>Annual consumption/production (t)</td>
<td>11 000</td>
</tr>
<tr>
<td>Material utilization (%)</td>
<td>100</td>
</tr>
<tr>
<td>Peak capacity factor (%)</td>
<td>100</td>
</tr>
</tbody>
</table>

optimization. Another option to increase algae productivity in low light conditions is to seasonally change the algal strain. In periods with low light, cultivation could be performed heterotrophically, by providing organic carbon for algae energy source. In a pulp and paper mill, the carbohydrates can be produced from e.g. waste fibre, or hemicellulose extracted from wood chips.

The choice of algal strain has a significant effect on biorefinery operation and it is subject to optimization. Significant algal strain properties that affect the biorefinery process applicability and general process design include the ability to grow in digestion effluent, dewaterability, growth rate in planned conditions and the content of desired end products.

Calculated photobioreactor size in the case study \(24 000 \text{ m}^3\) is greater than in any known installation: largest current algal photobioreactors have volume in the order of \(600 \text{ m}^3\) and land area of 1.2 ha [e.g. 46]. Assuming suggestive net areal productivity of \(0.048 \text{ kg m}^{-2} \text{ d}^{-1}\) [47], the plant area would be 31 ha. The simulated production is however significantly smaller than the pulp and paper production in the case study, which is in the order of 5000 t d\(^{-1}\); peak fertilizer flow is approximately 1% and algae growth only 0.3% of this amount. Calculated product flows and the plant size are dimensioned for maximum input flow utilization, but the biorefinery could also be built smaller. Experimental data on algae productivity in a large-scale, continuous-mode photobioreactors is yet required to verify the size estimation and to act as more reliable input data for economic calculations.

3.2. Mill integration

The proposed biorefinery would consume secondary streams from the pulp and paper mill, and in addition generate streams that could be utilized on the site: potential energy content in the produced methane corresponds to 10% of what is consumed in the case study paper machines as propane, and the daily oxygen production in cultivation is approximately 20% of the current oxygen production at the case study mill. Carbon dioxide consumption in algae cultivation is however very small in comparison to flue gas flows: used CO\(_2\) amount equals to less than one percent of what would be available on the site, but on the other hand the CO\(_2\) consumption is large enough to handle all carbon dioxide produced in digestion: nearly 40% of the demand could be fulfilled with the CO\(_2\) in the biogas.
The results of the study may be generalized to other similar systems, but the optimal biorefinery configuration may vary with different boundary conditions. Excess heat and carbon dioxide is available from many industrial plants, and the lacking nutrients could be supplied from for example municipal wastewaters. Conversely, a part of the presented process is suitable for biological wastewater treatment plants with an aerobic treatment process, but if other inputs such as ash, heat and carbon dioxide are not present, technical feasibility and product yields might be remarkably different from the studied case.

3.3. Biorefinery location

Table 4 displays how the choice of mill location affects algal growth: four different locations are chosen from countries that have significant pulp and paper industry and that represent different regions of the World. In this evaluation all input variables other than irradiance are kept constant. Algae production duration curves for the chosen locations are displayed in Figure 5: maximum growth rates are all on a similar level, but irradiance variation during the rest of the year creates a gap in algal productivity.

Even though algal growth is highly affected by variation in irradiance, methane and fertilizer production are more stable: annual methane and fertilizer production in São Paulo would be 14% and 6% higher than in Helsinki, with the same equipment. Input material is utilized more efficiently in areas where greater algal growth is attained, but some material remains unutilized due to production variance. Excess digestion effluent still contain nutrients, which can be recovered for example by precipitation and then added to the fertilizer.

The installmment in São Paulo seems most promising of the investigated alternatives, with regards to installed capacity utilization. Other parameters such as product markets, logistics, financial support mechanisms and political situation also affect the possible biorefinery placement. Hence, economic analysis that takes into account all these effects is required.

4. Conclusions

Presented biorefinery process seems technically viable in the light of mass balances and sensitivity analyses. Nutrients are efficiently circulated for algae production and finally utilized in fertilizer. Methane and oxygen production are moderate in comparison to existing consumption at the pulp and paper mill, whereas carbon dioxide utilization is very low in comparison to flue gas availability. Results indicate that the algal growth potential is sensitive to light and nutrient availability in cultivation. Therefore the analysis of feedstocks and optimization of algal strain are crucial in order to meet requirements set by the algae and the desired end products. Seasonal variation in irradiance results in remarkable changes in lipid production, but methane and fertilizer are less affected. Nutrient content in produced fertilizer is comparable to commercial organic fertilizers. Proposed process can likely be generalized to other process industry and wastewater treatment plants, given that required inputs are provided.

To further verify the presented concept, detailed energy consumption analysis, plant runtime optimization, economic analysis under different product price scenarios, and an environmental assessment are required. Furthermore, acquiring pilot-scale data in co-operation with experimental phycologists and process engineers is necessary.

Acknowledgements

This research was conducted in the BioRefineTech research program coordinated by Cursor Oy, with funding from Southern Finland European Regional Development Fund (ERDF) Programme Unit given out by South Finland EU Office.

References

Table 4: Effect of mill location to annual biorefinery production and input material utilization.

<table>
<thead>
<tr>
<th>Country</th>
<th>City</th>
<th>Latitude</th>
<th>Annual production</th>
<th>Peak capacity factor</th>
<th>Digestion effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finland</td>
<td>Helsinki</td>
<td>☎ 60</td>
<td>480 t lipids 550 t methane 1400 t fertilizer 18 000 t</td>
<td>% 89 91 93 70</td>
<td>% 47 57 79 79</td>
</tr>
<tr>
<td>Germany</td>
<td>Stuttgart</td>
<td>☎ 49</td>
<td>660 t 1400 t 18 000 t 18 000 t</td>
<td>10.1016/j.cherd.2013.02.006</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>Shanghai</td>
<td>☎ 31</td>
<td>810 t 1500 t 18 000 t 18 000 t</td>
<td>10.1016/j.cherd.2013.02.006</td>
<td></td>
</tr>
<tr>
<td>Brazil</td>
<td>São Paulo</td>
<td>☎ 24</td>
<td>95 t 1600 t 19 000 t 19 000 t</td>
<td>10.1016/j.cherd.2013.02.006</td>
<td></td>
</tr>
</tbody>
</table>

8


