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Introduction to Ammonia Production

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Introduction to Ammonia Production

Ammonia is critical in the manufacturing of fertilizers, and is one of the largest-volume synthetic chemicals produced in the world. This article explores the evolution of ammonia production and describes the

current manufacturing technologies.

Most people associate the pungent smell of ammonia (NH_3) with cleaners or smelling salts. However, the use of ammonia in these two products represents only a small fraction of the total global ammonia production, which was around 176 million metric tons in 2014 *(1)*. To appreciate where the industry and technology are today, let's first take a look at how we got here.

Ammonia has been known for more than 200 years. Joseph Priestley, an English chemist, first isolated gaseous ammonia in 1774. Its composition was ascertained by French chemist Claude Louis Berthollet in 1785. In 1898, Adolph Frank and Nikodem Caro found that N_2 could be fixed by calcium carbide to form calcium cyanamide, which could then be hydrolyzed with water to form ammonia *(2)*:

$$CaO + 3C \leftrightarrow CaC_2 + CO$$

$$CaC_2 + N_2 \leftrightarrow CaCN_2 + C$$

$CaCN_2 + 3H_2O \leftrightarrow CaCO_3 + 2NH_3$

The production of significant quantities of ammonia using the cyanamide process did not occur until the early 20th century. Because this process required large amounts of energy, scientists focused their efforts on reducing energy requirements.

German chemist Fritz Haber performed some of the most important work in the development of the modern ammonia industry. Working with a student at the Univ. of Karlsruhe, he synthesized ammonia in the laboratory from N_2 and H_2.

Meanwhile, Walther Nernst, a professor of physical chemistry at the Univ. of Berlin, developed a process to make ammonia by passing a mixture of N_2 and H_2 across an iron catalyst at 1,000°C and 75 barg pressure. He was able to produce larger quantities of ammonia at this pressure than earlier experiments by Haber and others at atmospheric pressure. However, Nernst concluded that the process was not feasible because it was difficult or almost impossible (at that time) to produce large equipment capable of operating at that pressure.

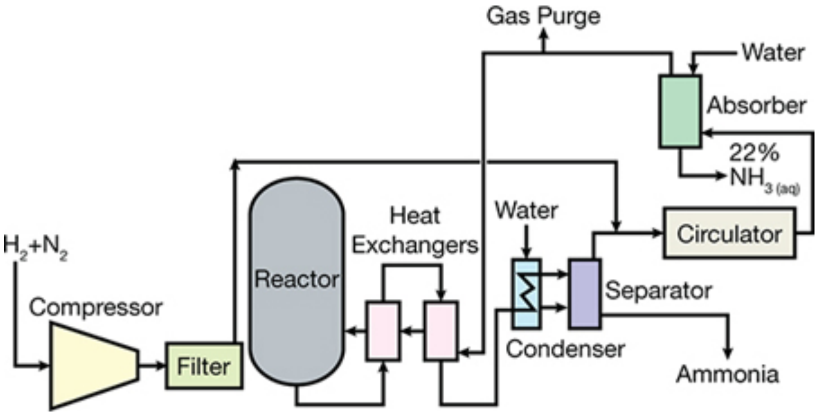
Nonetheless, both Haber and Nernst pursued the high-pressure route to produce ammonia over a catalyst. Haber finally developed a process for producing commercial quantities of ammonia, and in 1906 he was able to achieve a 6% ammonia concentration in a reactor loaded with an osmium catalyst. This is generally recognized as the turning point in the development of a practical process for the production of ammonia in commercial quantities.

Haber realized that the amount of ammonia formed in a single pass through a converter was far too low to be of commercial interest. To produce more ammonia from the makeup gas, he proposed a recycle system, and received a patent for the concept. Haber's recycle idea changed the perception of process engineering as static in favor of a more dynamic approach.

In addition to the chemical reaction equilibrium, Haber recognized that reaction rate was a determining factor. Instead of simple yield in a once-through process, he concentrated on space-time yield in a system with recycle.

BASF purchased Haber's patents and started development of a commercial process. After testing more than 2,500 different catalysts, Carl Bosch, Alvin Mittasch, and other BASF chemists developed a promoted iron catalyst for the production of ammonia in 1910. Developing equipment that could withstand the necessary high temperatures and pressure was an even more difficult task. An early mild steel reactor lasted only 80 hours before failure due to decarbonization. Lining mild steel reactors with soft iron (which was not vulnerable to decarbonization) and adding grooves between the two liners to release hydrogen that had diffused through the soft iron liner solved this problem. Other major challenges included designing a heat exchanger to bring the inlet gas to reaction temperatures and cool the exit gas, and devising a method to bring the catalyst to reaction temperature.

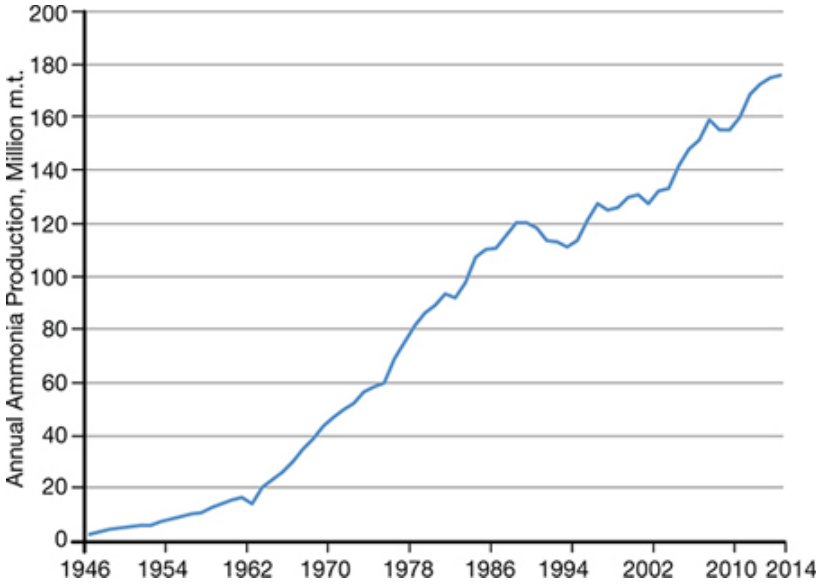
The first commercial ammonia plant based on the Haber-Bosch process was built by BASF at Oppau, Germany. The plant went on-stream on Sept. 9, 1913, with a production capacity of 30 m.t./day.



▲**Figure 1.** This is a simplified flowsheet of the first commercial ammonia plant by BASF.

Figure 1 is a flowsheet of the first commercial ammonia plant. The reactor contained an internal heat exchanger in addition to those shown on the schematic.

Global production rates



▲**Figure 2.** Worldwide ammonia production has steadily increased from 1946 to 2014.

Ammonia production has become one of the most important industries in the world. Without the crop yield made possible by ammonia-based fertilizers and chemicals, the global population would be at least two to three billion less than it is today *(3)*. Ammonia production has increased steadily since 1946 (Figure 2), and it is estimated that the annual production of ammonia is worth more than $100 billion, with some plants producing more than 3,000 m.t./day of NH_3.

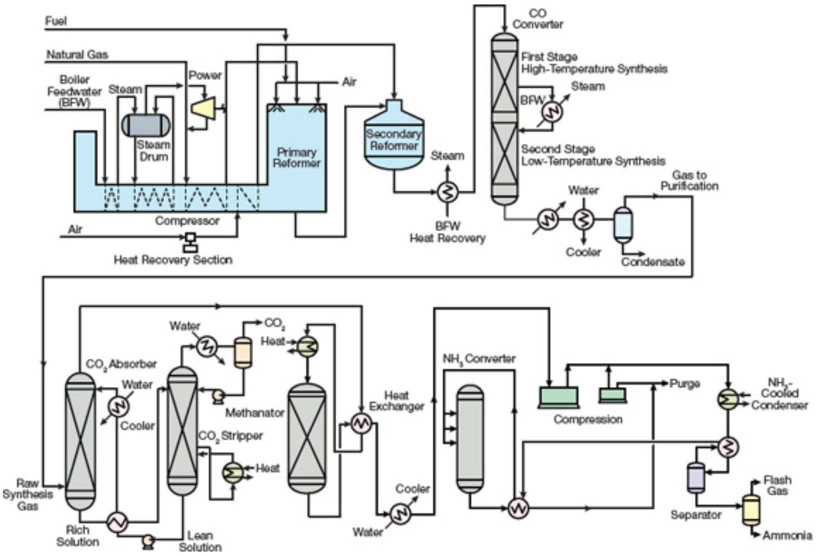
In 1983, on the occasion of the 75th anniversary of AIChE's founding, a blue ribbon panel of distinguished chemical engineers named what they believed to be the world's ten greatest chemical engineering achievements *(4)*. Embracing such feats as wonder drugs, synthetic fibers, and atomic energy, the citation also included the breakthrough that permitted the production of large quantities of ammonia in compact, single-unit plants.

Within the past decades, chemical engineers have succeeded in creating processes that make vast amounts of ammonia at relatively low costs. As recently as 80 years ago, the total annual production of synthesized ammonia was just over 300,000 m.t. Thanks to chemical engineering breakthroughs, one modern ammonia plant can produce more than 750,000 m.t./yr.

Approximately 88% of ammonia made annually is consumed in the manufacturing of fertilizer. Most of the remainder goes into the production of formaldehyde. China produced about 32.6% of the global production in 2014, while Russia, India, and the U.S. produced 8.1%, 7.6%, and 6.4%, respectively *(1)*. While most of the global production of ammonia is based on steam reforming of natural gas, significant quantities are produced by coal gasification; most of the gasification plants are located in China.

Modern production processes

The tremendous increase in ammonia demand from 1950 to 1980 necessitated larger, more-energy-efficient plants. Those decades also saw a change in design philosophy. Until that time, an ammonia plant was regarded as an assembly of unrelated units, such as gas preparation, gas purification, gas compression, and ammonia synthesis. New innovations and an integral design tied process units together in the most effective and efficient ways.



▲**Figure 3.** KBR designed one of the first single-train, large-capacity ammonia plants.

In the mid-1960s, the American Oil Co. installed a single-converter ammonia plant engineered by M.W. Kellogg (MWK) at Texas City, TX, with a capacity of 544 m.t./day. The single-train design concept (Figure 3) was so revolutionary that it received the Kirkpatrick Chemical Engineering Achievement Award in 1967.

The plant used a four-case centrifugal compressor to compress the syngas to a pressure of 152 bar, and final compression to an operating pressure of 324 bar occurred in a reciprocating compressor. Centrifugal compressors for the synthesis loop and refrigeration services were also implemented, which provided significant cost savings.

The key differences between the MWK process and the processes used in previous ammonia plants included:

- using a centrifugal compressor as part of the synthesis gas compression
- maximizing the recovery of waste heat from the process
- generating steam from the waste heat for use in steam turbine drivers
- using the refrigeration compressor for rundown and atmospheric refrigeration.

An integrated scheme that balanced energy consumption, energy production, equipment size, and catalyst volumes was incorporated throughout the plant.

Most plants built between 1963 and 1993 had large single-train designs with synthesis gas production at 25–35 bar and ammonia synthesis at 150–200 bar. Another variation by Braun (now KBR) offered slight modifications to the basic design. The Braun Purifier process plants utilized a primary or tubular reformer with a low outlet temperature and high methane leakage to reduce the size and cost of the reformer. Excess air was added to the secondary reformer to reduce the methane content of the primary reformer exit stream to 1–2%. Excess nitrogen and other impurities were removed downstream of the methanator. Because the synthesis gas was essentially free of impurities, two axial-flow ammonia converters were used to achieve a high ammonia conversion.

Some recently built plants have a synthesis gas generation system with only one reformer (no secondary reformer), a pressure-swing adsorption (PSA) system for H_2 recovery, and an air separation plant as the source of N_2. Improvements in converter design, such as radial and horizontal catalyst beds, internal heat exchangers, and synthesis gas treatment, helped increase ammonia concentrations exiting the synthesis converter from about 12% to 19–21%. A higher conversion per pass, along with more-efficient turbines and compressors, further reduced energy consumption. More-efficient CO_2 removal solutions, such as potassium carbonate and methyldiethanolamine (MDEA), have contributed to improved energy efficiency. Most modern plants can produce ammonia with an energy consumption of 28 GJ/m.t.

In addition to the design, mechanical, and metallurgical improvements made during this time, the operating pressure of the synthesis loop was significantly reduced. When the first single-train plant was built in the 1960s, it contained a high-pressure synthesis loop. In 1962, MWK received an inquiry from Imperial

Chemical Industries (ICI) for a proposal to build a 544-m.t./day plant at their Severnside site. MWK proposed a 152-bar synthesis loop instead of a 324-bar loop.

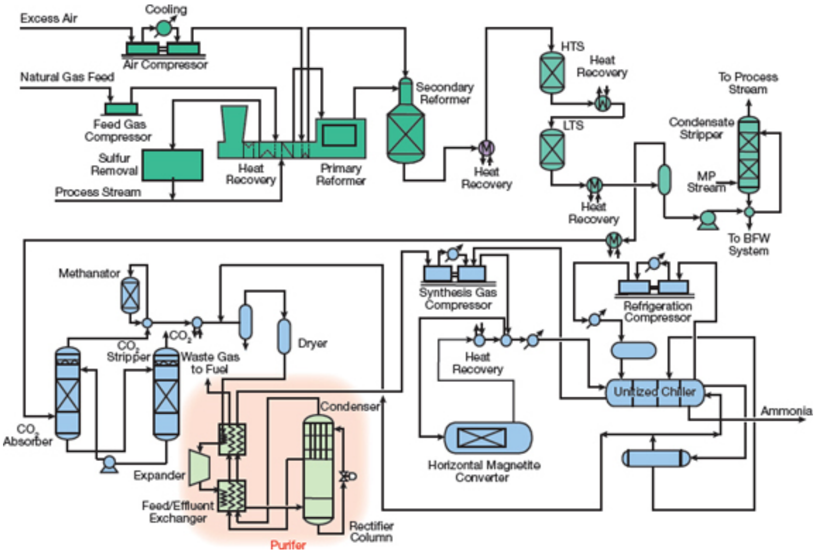
Because the development of kinetic data for the ammonia reaction at 152 bar would take more time than MWK had to respond to the ICI inquiry, they contacted Haldor Topsøe to support their plans. Topsøe had data covering the entire pressure range of interest to MWK. In addition, they had a computer program for calculating the quantity of catalyst that was required at the lower operating pressure. Even though ICI chose Bechtel to design the plant, MWK was able to develop a flowsheet for a 544-m.t./day design with centrifugal compressors and a low-pressure synthesis loop, which some people consider the single most important event in the development of the single-train ammonia plant.

Approximately twice as much catalyst was required at 152 bar as at 324 bar, an increase that seemed economically feasible. Although the converter would need twice the volume, the lower operating pressure would reduce the required thickness of the pressure shell. As a result, the weight of metal required for the converter plus the catalyst remained about the same. The lower-pressure synthesis loop also allowed the use of centrifugal compressors instead of reciprocating compressors. Another improvement was recovering heat to generate high-pressure steam for steam turbine drives.

Plant designs in the 21st century

During the first few years of the 21st century, many improvements were made in ammonia plant technology that allow existing plants to increase production rates and new plants to be built with larger and larger capacities. Competition between technology suppliers is quite fierce. Three technology licensors — KBR (Kellogg Brown and Root), Haldor Topsøe, and ThyssenKrupp Industrial Solutions (TKIS) —

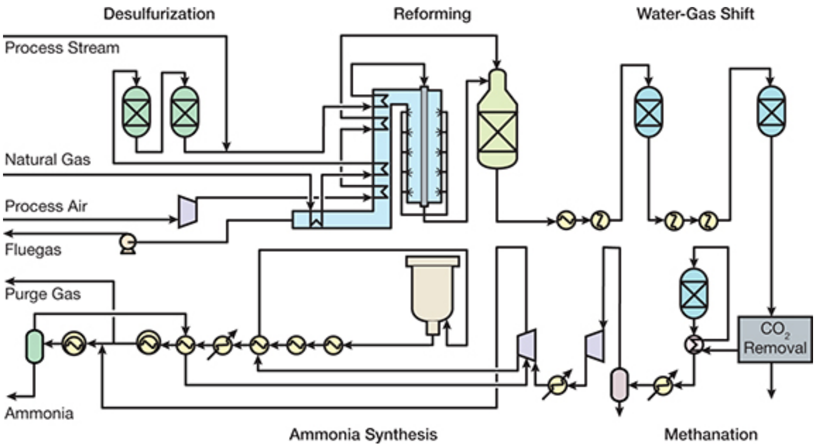
design, is a market leader in revamps of existing plants.



▲**Figure 4.** Modern ammonia plants designed by KBR employ its proprietary Purifier design.

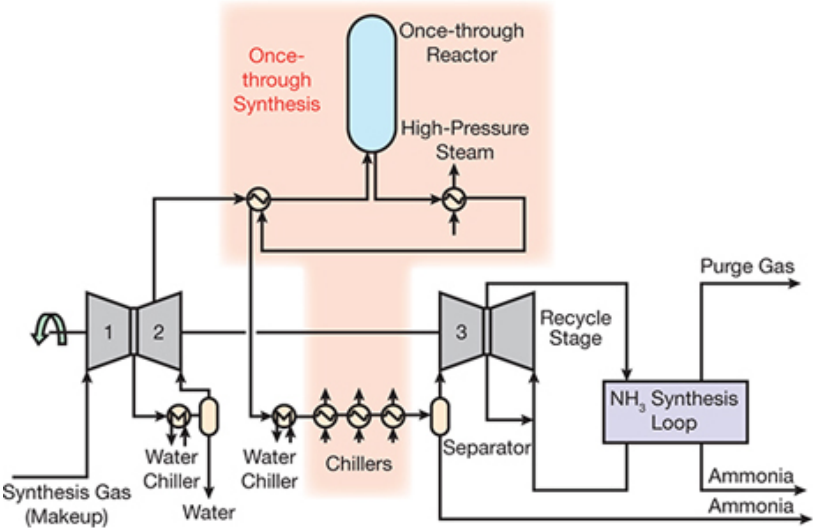
Most of the ammonia plants recently designed by KBR utilize its Purifier process (Figure 4), which combines low-severity reforming in the primary reformer, a liquid N_2 wash purifier downstream of the methanator to remove impurities and adjust the H_2:N_2 ratio, a proprietary waste-heat boiler design, a unitized chiller, and a horizontal ammonia synthesis converter.

Depending on the configuration of the plant, energy consumption can be as low as 28 GJ/m.t. Because the secondary reformer uses excess air, the primary reformer can be smaller than in conventional designs. The cryogenic purifier (shown in Figure 4 in light green with a light orange background), which consists of an expander, condenser, feed/effluent exchanger, and rectifier column, removes impurities such as CO, CH_4, and argon from the synthesis gas while adjusting the H_2:N_2 ratio of the makeup gas in the ammonia loop to the optimum level. The ammonia concentration exiting the low-pressure-drop horizontal converter is 20–21%, which reduces energy requirements for the recycle compressor. KBR also offers a low-pressure ammonia loop that employs a combination of magnetite catalyst and its proprietary ruthenium catalyst.



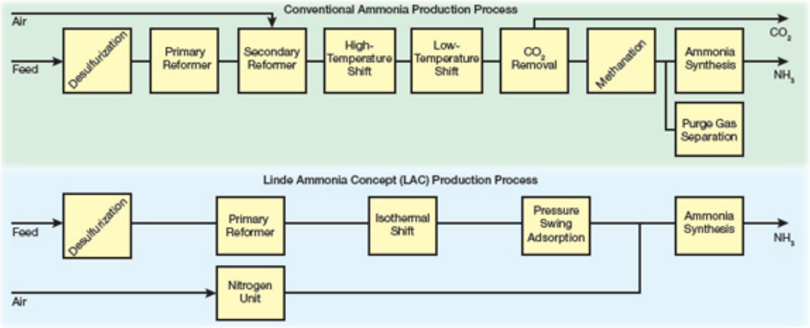
▲**Figure 5.** Haldor Topsøe offers an ammonia plant design that has a proprietary side-fired reformer in which radiant burners supply heat for the reforming reaction.

The syngas generation section (or front end) of a Haldor Topsøe-designed plant (Figure 5) is quite traditional with the exception of its proprietary side-fired reformer, which uses radiant burners to supply heat for the reforming reaction. Haldor Topsøe also offers a proprietary iron-based synthesis catalyst, radial-flow converters consisting of one, two, or three beds, and a proprietary bayonet-tube waste-heat boiler. More recent developments include the S-300 and S-350 converter designs. The S-300 converter is a three-bed radial-flow configuration with internal heat exchangers, while the S-350 design combines an S-300 converter with an S-50 single-bed design with waste-heat recovery between converters to maximize ammonia conversion.



▲**Figure 6.** ThyssenKrupp's dual-pressure synthesis loop design features a once-through reactor between syngas compressors.

ThyssenKrupp offers a conventional plant (Figure 6) with a unique secondary reformer design, a proprietary waste-heat boiler, radial-flow converters, and a dual-pressure ammonia synthesis loop. Today, a production rate of 3,300 m.t./day can be achieved using the TKIS dual-pressure process.

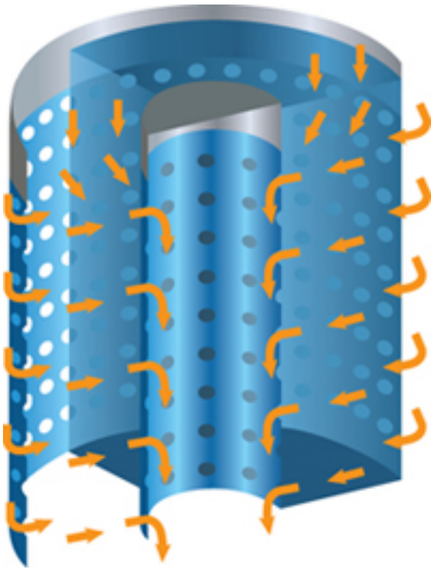


▲**Figure 7.** The Linde Ammonia Concept (LAC) features a pressure-swing adsorption unit for high-purity hydrogen production and an air separation unit for high-purity nitrogen production.

The Linde Ammonia Concept (LAC) is an established technology process scheme with over 25 years of operating experience in plants with capacities from 200 m.t./day to over 1,750 m.t./day. The LAC process scheme (Figure 7) replaces the costly and complex front end of a conventional ammonia plant with two well-proven, reliable process units:

- production of ultra-high-purity hydrogen from a steam-methane reformer with PSA purification
- production of ultra-high-purity nitrogen by a cryogenic nitrogen generation unit, also

known as an air separation unit (ASU).



▲**Figure 8.** Ammonia Casale's process employs a catalyst bed that harnesses axial-radial technology, which has a lower pressure drop and higher efficiency than standard catalyst beds.

Ammonia Casale's plant design has a production rate of 2,000 m.t./day. One of the key features of this design is axial-radial technology in the catalyst bed (Figure 8). In an axial-radial catalyst bed, most of the synthesis gas passes through the catalyst bed in a radial direction, creating a very low pressure drop. The rest of the gas passes down through a top layer of catalyst in an axial direction, eliminating the need for a top cover on the catalyst bed. Casale's axial-radial catalyst bed technology is used in both high-temperature and low-temperature shift converters, as well as in the synthesis converter.

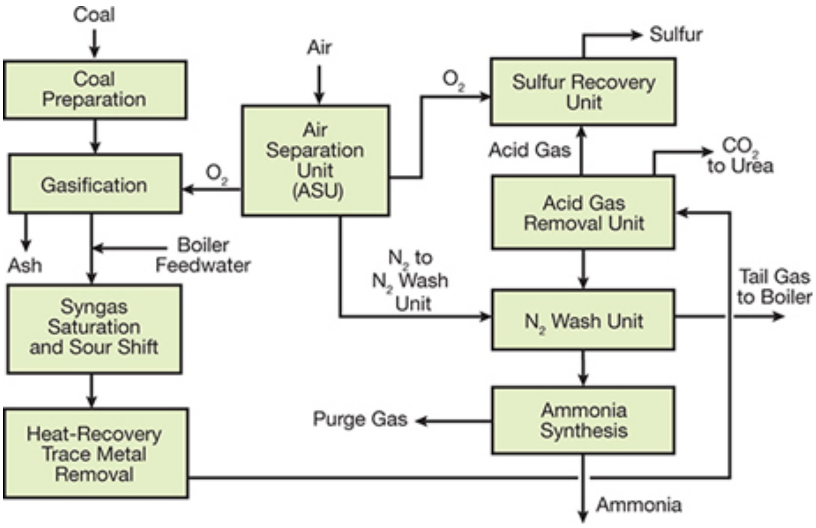
Other technologies

Some technology suppliers have offered gas-heated reformers (GHRs) for the production of ammonia in small-capacity plants or for capacity increases. Unlike conventionally designed plants that use a primary reformer and secondary reformer operating in series, plants with GHRs use the hot process gas from the secondary reformer to supply heat to the primary reformer. This reduces the size of the primary reformer and eliminates CO_2 emissions from the primary reformer stack, making the process more environmentally friendly.

Even though some ammonia producers

advocate for distributed production of ammonia in small ammonia plants, most companies prefer to build large facilities near cheap raw material sources and transport the product by ship, rail, or pipeline to the consumers.

Ammonia from coal



▲**Figure 9.** China produces most of its ammonia from coal.

China produces more ammonia than any other country, and produces the majority of its ammonia from coal (Figure 9).

The basic processing units in a coal-based ammonia plant are the ASU for the separation of O_2 and N_2 from air, the gasifier, the sour gas shift (SGS) unit, the acid gas removal unit (AGRU), and the ammonia synthesis unit. Oxygen from the ASU is fed to the gasifier to convert coal into synthesis gas (H_2, CO, CO_2) and CH_4. There are many gasifier designs, but most modern gasifiers are based on fluidized beds that operate above atmospheric pressure and have the ability to utilize different coal feeds. Depending on the design, CO levels of 30–60% by volume may be produced.

After gasification, any particulate matter in the synthesis gas is removed and steam is added to the SGS unit. The SGS process typically utilizes a cobalt and molybdenum (CoMo) catalyst specially designed for operation in a sulfur environment.

After reducing the CO concentration in the synthesis gas to less than 1 vol%, the syngas is fed to an AGRU, where a chilled methanol scrubbing solution (*e.g.*, Rectisol) removes CO_2 and sulfur from the synthesis gas. The CO_2 overhead is either vented or fed to a urea plant. The sulfur outlet stream is fed to a sulfur recover unit (SRU).

Syngas that passes through the AGRU is typically purified by one of two methods:

- a nitrogen wash unit to remove residual CO and CH_4 from the syngas before it is fed to the synthesis loop
- a PSA system for CO and CH_4 removal.

Closing thoughts

During the past 60 years, ammonia process technology has improved drastically. Plant layouts evolved from multi-train designs, often with different numbers of trains in the front end and synthesis loop, to single-train designs. Synthesis gas preparation in the front end of the plant increased from atmospheric pressure to 30–50 barg pressure. Capacities increased from 100 m.t./day to as much as 3,300 m.t./day in a single train.

Energy efficiencies have improved as well — from consumptions well above 60 GJ/m.t. of ammonia in coke-based plants to 40–50 GJ/m.t. in the first natural-gas-based plants to 30–40 GJ/m.t. in the first single-train plants. Modern plants have added heat recovery by steam production at pressures as high as 125 barg in both the syngas preparation section and the synthesis loop.

In terms of process equipment, there has been a shift from reciprocating compressors to centrifugal compressors. An internal heat exchanger has been implemented in the synthesis converter to increase conversion of H_2 and N_2 to NH_3. Designers have tapped into hydrogen recovery from purge gas (in units such as PSA systems) to enhance production or reduce the plant energy consumption. Designers have also implemented hot feed gas desulfurization systems. There have been significant improvements in the catalysts used in reforming, shift conversion, methanation, and ammonia synthesis.

To improve process control and safety, distributed control systems (DCSs) for advanced process control, as well as safety-instrumented systems (SISs), are now standard in ammonia plants. Before any process goes online, hazard and operability (HAZOP) studies and layer of protection analyses (LOPAs) are performed. Advances in training simulators and education practices ensure that operators and engineers can perform their duties safely and effectively.

These are just a few of the thousands of improvements in technology and safety that have been implemented to make the ammonia industry one of the most productive and safe industries in the world.

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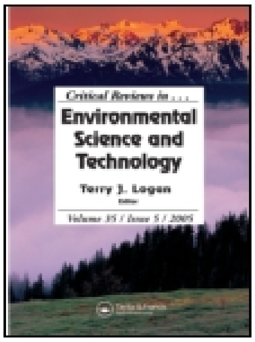

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Recent Trends in Leather Making: Processes, Problems, and Pathways

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Recent Trends in Leather Making: Processes, Problems, and Pathways

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Leather processing has emerged as an important economic activity in several developing countries. Awareness of environmental problems has increased considerably and during recent years protecting environment has become a global issue. Currently the leather processing industry is going through a phase change due to global environmental regulations. The article summarizes the current leather processing methods with their rationale and environmental problems. It has been revealed that pretanning and tanning processes contribute 80–90% of the total pollution load (BOD, COD, TS, TDS, Cr, S^{2-}, sludge, etc.). Further, toxic gases like ammonia and hydrogen sulfide are also emitted. Volatile organic compounds, heavy metals, and carcinogenic arylamines from posttanning and finishing operations are also creating severe concern. Apart from this, a great deal of solid wastes like lime sludge from tannery and chrome sludge from effluent treatment plants are being generated. Advanced processing techniques as well as effluent treatment strategies for combating environmental and human health risks are reviewed in detail. The leather processing industry in various countries, however, is facing a serious challenge from the public and government. This is in spite of the implementation of several advanced processing techniques and treatment systems. Hence, there is a need to revamp leather processing methods anew for the sustainability of leather industry. Some of the novel concepts in leather processing are briefly mentioned and discussed.

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KEY WORDS: chemical oxygen demand, dehairing, effluent treatment, enzyme, fiber opening, leather processing, pollution, sludge, tanning, total solids

I. INTRODUCTION

A. Leather Industry: A Global Perspective

Leather is a unique commodity that links the rural farmer to the fashion world. Leather as a natural material offers numerous advantages over synthetics, namely, aesthetic appeal, feel, texture, and breathability. Major product applications for leather are leather goods, garments, and footwear. More than 60% of the leathers produced are being converted to footwear (Taeger, 1996). The annual global trade in leather sector is estimated as US$70,000,000,000 (ITC, 1999). The United States, Germany, and other European countries remain major importers of leather products. Countries such as China, India, Thailand, and Indonesia dominate leather and leather products exports. The demand for leather and leather products is on the rise and is independent of supply.

Leather processing has emerged as an important economic activity in several developing countries that are dependent on agricultural economy. It has been estimated that about 1.67×10^9 m^2 of leather is being made annually in the world (FAO, 2001). The bulk of the leather production is carried out in developing economies, partially because of the high labor intensity of the processes involved in the conversion of hides and skins into leather. India is a major player in the global leather trade. Leather has assumed importance as an opportunity sector for social development, employment generation, and export realization. Leather is a thrust area in national planning for the development of India. The Indian leather industry has evolved over nearly two centuries. Currently, the overall share of India in the global leather trade is around 3% (ITC, 1999). There are about 2100 tanneries located in India, with a processing 0.9×10^6 tons of rawhides and skins (Velappan and Muralidharan, 2001). Major tannery clusters in India are located in the states of Tamil Nadu, West Bengal, Uttar Pradesh, and Punjab.

B. Leather and Environment: A Challenging Issue

The global environment is degrading due to socioeconomic activities of mankind. Environmental protection and sustainable development are gaining public importance. Industries that cause adverse changes to the immediate environment are being challenged by the society. The global leather industry is one among them.

Leather processing is one of the earliest industrial activities taken up by humans. The processes used in the manufacture of leather in several developing countries remain traditional and are often not optimized for chemical and water usage. Leather making can also be called an activity that helps in utilizing potential wastes (Germann, 1999; Sykes, 1996). The utilization of by-products of the meat industry, namely, hides/skins, is achieved by tanning using basic chromium sulfate (BCS) or vegetable tannins. This, however, is a simplistic view. A more detailed analysis of environmental consequences of the tanning industry is critical. The industry has gained a negative image in the society with respect to pollution. Leather processing activity is therefore facing a serious challenge and there is public outcry against the industry. This is in spite of the leather industry having made traceable and visible impacts in the socioeconomic area through both employment generation and export earnings.

II. LEATHER PROCESSING: SOURCE OF POLLUTION

Leather processing involves a series of operations, as shown in the flow diagram in Figure 1. The operations involved in leather processing may be classified in three groups: pretanning or beamhouse operations, tanning, and posttanning as detailed by Ramasami and Prasad (1991). Pretanning

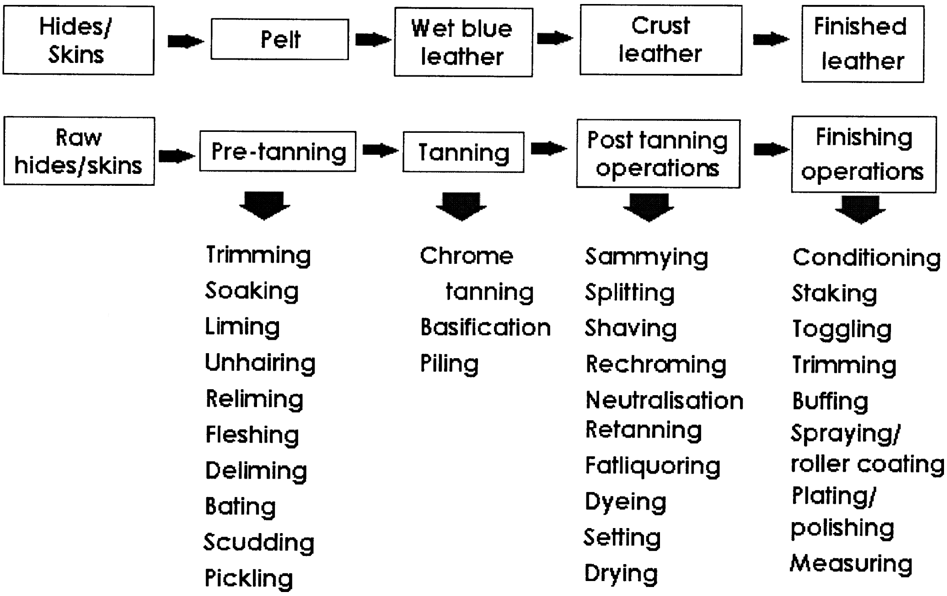

FIGURE 1. Various unit processes and operations in leather processing (Saravanabhavan et al., 2003).

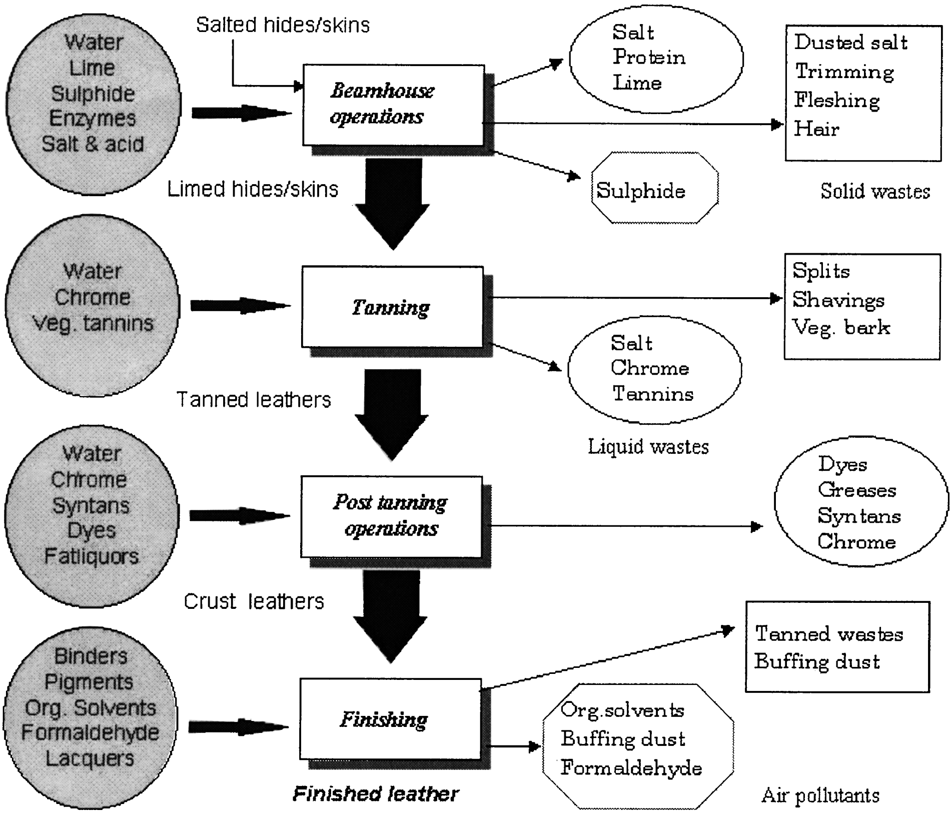

FIGURE 2. Inflow–outflow diagram for leather processing (Rao et al., 2003).

operations aim at cleaning hides/skins, tanning stabilizes the skin/hide matrix permanently, and aesthetic values are added during post tanning and finishing operations.

The various chemical inputs into leather processing are given in Figure 2 (Rao and Ramasami, 1997). Water is the main medium of transport for the chemicals in leather processing. The leather industry uses about 35–40 L of water/kg of hide processed (Ramasami and Prasad, 1991). With the present annual processing capacity of 0.9×10^9 kg of hides and skins in India, it is estimated that nearly 30 to 40×10^9 L of liquid effluent is generated annually. This gives rise to two major problems for the leather industry: the availability of good quality water, and the need for treatment of such large quantities of effluent. The extent of pollution load emanating from the leather processing using conventional methods can be assessed from the emission factors for various operations as indicated in Table 1 (Ramasami et al., 1998). Nearly 70% of the emission loads of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS) emanates from the pretanning operations (Ramasami et al., 1999a, 1999b). Almost the entire

TABLE 1. Typical Range of Emission Factors for Conventional Leather Processing

Parameters	Soaking	Liming	Deliming	Pickling	Vegetable tanning	Chrome tanning	Dyeing and fatliquoring	Composite (includes washing)
Volume of effluent	6–9	3–4	1–2	0.5–1.0	0.5–2	1–2	1–2	30–40
BOD	6–24	15–40	1–6	0.2–0.7	3–18	0.3–1.6	1–4	30–120
COD	18–60	30–100	2.5–14	0.5–3	7.5–40	1–5	2–14	75–320
Total solids	200–500	90–200	4–20	17–70	12–60	30–120	4–20	450–1000
Dissolved solids	190–400	70–120	2.5–10	17–70	10–50	30–100	3–15	300–800
Suspended solids	15–60	15–80	1.5–8	0.5–3	2–10	1–5	0.6–2	60–160
Chloride as Cl^-	90–250	10–30	1–4	10–30	0.5–2.5	15–50	0.5–2	150–350
Total chromium as Cr	—	—	—	—	—	2–10	0.04–0.2	3–10

Note. All values expressed in kg/ton of hide or skin processed; These were obtained from the formula (concentration × volume of effluent)/ton of leather processed (Thanikaivelan et al., 2004, unpublished).

quantity of sulfide discharge is from the dehairing operations (Steven, 1983). Chrome tanning activity is associated with large discharge of chromium and sulfate ions (Rao et al., 1983).

A. Pretanning

1. SOAKING

The starting material for leather processing, in most cases, is rawhide or skin, which had been preserved temporarily by the addition of common salt. Soaking aims at reversal of cured hides and skins to near the status of the freshly flayed condition, in terms of dimension and composition. Large amounts of water and small amounts of preservatives/wetting agents are used at this stage. The common salt, when removed from the skin during soaking, constitutes a major source of pollution from tanneries (Ludvik and Orlita, 1986). Because the dissolved sodium chloride is not easily treated and removed from wastewater, the discharge of tannery wastewater onto land leads to significant addition of salinity to the soil (Daniels, 1997). The soak liquor is characterized by high TDS and chloride content (Ramasami et al., 1999b). Currently, the problem is tackled by the segregation of soak liquors for salt recovery through solar evaporation pans. Soak liquor also contains salt soluble proteins and other organic materials, which contribute marginally to the BOD and COD load. Through judicious choice of methods, however, it may be possible to minimize the BOD and COD loads. Obnoxious smell and ammoniacal odor emanating from degraded protein are also associated with spent soak liquor.

2. LIMING

One of the most important pretanning operations is liming. The main objective of liming is removal of hair, flesh, and splitting up of fiber bundles by chemical and physical means (Ramasami and Prasad, 1991). Hair can be either digested (using lime and sodium sulfide) or mechanically removed after loosening by chemical means. Flesh, being a loose, unstructured, and noncompact material, has to be separated from leather-making material, corium (middle layer of skin made up of a protein, collagen, in naturally woven fiber bundles form), by the action of hydrostatic pressure and then is removed using a fleshing machine or knife. In this operation, lime and sodium sulfide are used along with substantial quantities of water (Money, 1996). Lime increases the pelt pH to 12–13 and also causes osmotic swelling due to ionic imbalances built up in the matrix (Bienkiewicz, 1983). Swelling causes changes in dimension and charge characteristics of the skin/hide. The skin/hide matrix essentially becomes anionic, in other words, a cation exchanger. The hydrostatic pressure built up enhances the splitting up of fiber bundles, separation of unwanted interfibrillary materials, and easy removal of flesh (Ramasami et al., 1999a). Moreover, the combined action of S^{-2} and OH^- ions helps to degrade hair protein by nucleophilic displacement reaction at disulfide bonds, as reported by Windus and Showell (1968).

Significant amounts of chemicals are used during pretanning. Optimum amounts of chemicals need to be used to reduce the TDS, BOD, and COD loads. Liming operations lead to not only wastewater containing significant amounts of BOD, TDS and S^{2-} but also substantial quantities of solid wastes containing lime sludge, fleshing and hair (Ramasami and Prasad, 1991). Sodium sulfide, a good reducing agent, interferes in the oxidation of organic wastes and contributes significantly to the BOD and COD concentrations in wastewater (Steven, 1983). The extensive use of sulfide yields unfavorable consequences on environment and the efficacy of effuent treatment plants (ETPs) (Bailey et al., 1982).

3. DELIMING

The pH of the limed pelt is highly alkaline. The reduction of pH or alkalinity needs to be gradual due to several reasons as given by Ramasami et al. (1999a), including: (a) The heat of neutralization of alkali and rate of heat dissipation should be very low, taking into account the heat sensitivity of the pelt; (b) the presence of sulfides in the pelt limits the pH conditions for the safe removal of lime, if the formation of hydrogen sulfide is to be avoided; and (c) the control of pH for optimum activity of bating enzymes used subsequently. Deliming agents based on weakly acidic salts like ammonium chloride and ammonium sulfate are used to neutralize lime after the hair and flesh have been removed from the skin (Ramasami and Prasad, 1991). It is now recognized that the use of nitrogen-bearing salts could affect the N:P:K ratios of soil (Dix, 2000; Ramasami, 1993). Nitrogen-based deliming agents are considered a long-term environmental threat (Huber and Satyendra, 1990). The resultant salts of this operation would in turn increase the amounts of COD and TDS (Ramasami et al., 1994).

4. BATING

The complete removal of unwanted interfibrillary materials and short hairs through the use of enzymatic applications is the objective of bating (Ramasami and Prasad, 1991). The majority of the commercial preparations of the enzymes used in bating are generally more effective in the pH range of 8.2 to 8.8 or 3.5 to 4.5. The liquid wastes from this operation contain usually small quantities of proteineous matter and other debris, which contribute to BOD and COD significantly. These loads could be minimized through careful choice of bating formulation (D'Souza and Vedarajan, 1997; Dederle et al., 1984).

5. PICKLING

Pickling is a process in which the partially anionic matrix is temporarily converted into a cationic matrix in order to prepare the stock for the subsequent chrome tanning operation (Bienkiewicz, 1983). It uses substantial quantities of sulfuric acid and sodium chloride. In this operation, the pH is adjusted to 2.5–2.8. In order to suppress osmotic swelling caused by acid addition, the concentration of sodium chloride is maintained at the required ionic strength (O'Flaherty et al., 1978). Excessive use of common salt and sulfuric acid, as carried out commonly during pickling operation, leads to significant COD as well as TDS loads (Ludvik, 1997; Prasad et al., 1981). In the case of vegetable tanning, the need for extensive pickling does not arise. It has now been established that sulfate ions in wastewater not only contribute to the TDS but also reduce the efficacies of ETPs (Rajamani, 1997; Ramasami et al., 1999a).

B. Tanning

Tanning is a process in which the leather-making protein is permanently stabilized against heat, enzymatic biodegradation, and thermomechanical stress (Ramasami, 2001). In commercial practice, vegetable and chrome tanning methods are widely used. The vegetable tanning method does not need the prior preparation stage of pickling and therefore the contributions to pollution load from sulfate salts are lower. Vegetable tannins, however, are known to be hard to biodegrade (Healy and Young, 1978), and hence wastes bearing vegetable tannins degrade slowly.

Among the various tanning systems, chrome tanning is the most commonly used tanning system in commercial practice due to its ability to produce softer, weightless, bright-shade leathers with high wet heat resistance in a shorter time frame. More than 90% of the leathers processed globally contain chromium (Covington, 1997a; Germann, 1995, 1999). In chrome tanning, the cationic matrix (pickled pelt) is treated with BCS. Diffusion of chromium(III) salts into the skin matrix at pH < 3.0 initially leads to ionic interactions (Rao et al., 1997). Over longer durations of tanning, readjustments in pH of the medium around 3.8–4.0 lead to irreversible binding of Cr(III) salts to the protein through coordinate covalent bonding (Shuttleworth, 1950). The addition of an alkali, sodium bicarbonate, not only increases the pH to the pK_a value of carboxy amino acids but also increases the basicity (Schorlemmer basicity, defined as the percentage of number of hydroxyl groups combined with one atom of chromium [Sharphouse, 1983]) of Cr(III) species (Venkatachalapathi et al., 1982). The interaction of chromium(III) salts with the protein matrix involves a complex array of chemical processes. At least two kinetic stages have been identified in the chrome tanning operation (Rao, 1991). The binding of chromium at the molecular level provides inter- and intrachain crosslinks along the triple helices, penta fibril, and fibrillar assemblies up to higher organizations of collagen (Covington, 1997a). Thus, the molecular mass of collagen may increase from 300,000 to $(300{,}000)n$ daltons where n is the number of collagen molecules interlocked through coordinate covalent interaction with chromium complexes. This increase in long-range order of the matrix would essentially result in increase in thermomechanical stress and to further desolvation due to the reduction in the interaction of water clusters around the protein functional groups (Gayatri et al., 1999).

BCS is a mixture of many molecular species such as octaaqua-μ-dihydroxochromium(III), octaaqua-μ-dioxochromium(III), hexaaqua-μ-dihydroxo-μ-sulfatochromium(III), and tetraaquahydroxosulfatochromium(III) (Rao et al., 1997). High kinetic lability and poor thermodynamic affinity of some of the species lead to poor uptake of chromium during chrome tanning. Depending on the manufacturing conditions, the uptake of BCS may vary (Chandrasekaran et al., 1999). When the uptake levels are low, higher amounts of chromium along with neutral salts are discharged, which increase the COD, TDS, and SO_4^{2-} content in the spent chrome liquor (Chandrasekaran et al., 1989). Although the oxidation state of chromium in the tanning salt is only trivalent, discharge norms do not often specify the redox states, because of the concerns of possible conversion of the trivalent state to the more toxic hexavalent form (Fathima et al., 2001; Bartlett and James, 1979). The spent chrome tanning solutions are sources of both TDS and chromium pollution, which need to be addressed.

C. Posttanning

Posttanning operations, in general, attempt the addition of aesthetic values and improvement of intrinsic properties of leather (Ramasami et al., 1999c). Rechroming, neutralization, retanning, dyeing, and fatliquoring form the major steps of posttanning operations (Ramasami and Prasad, 1991). Posttanning operations are carried out in a narrow pH range of 4.0–6.0 using a wide variety of proprietary formulated chemicals. It is now realized that posttanning processes contribute to neutral salts, COD, and heavy metal pollution (Simoncini and Sammarco, 1995). Wastewater from posttanning processes contains COD, TDS, and Cr in the range of 8.25, 10.7, and 0.12 kg/ton of leather processed, respectively (Ramasami et al., 1998). Additionally, azo dyes and biocides add to the toxic load of wastewater streams (BASF, 1998). The contributions to BOD, COD, and TDS loads in wastewater are significantly lower from the posttanning operations in comparison to the total discharge. It, however, is necessary to carry out treatability studies on the proprietary formulations so that nondegradable substances may be avoided.

D. Finishing

The pollution load and the volume of the effluent generated in finishing operations are not significant. This waste stream is characterized by the presence of polymeric binders, heavy-metal-based pigments, solvents, nitrocellulose, and other topcoat materials, as described by Greif (1990). The volume of effluent from these operations including washing is about 1–2 m^3/ton of rawhide processed (Langerwerf and Chandrababu, 1999). The air pollution related to use of formaldehyde, unreacted acrylic monomers, toxic-metal-based pigment formulations, and solvent-based top coats causes concern, as the bulk of the gaseous wastes is produced in this set of unit operations (Swarna et al., 1999; Corning et al., 1991; Deselinicu et al., 1997).

E. Solid Wastes

Apart from liquid and gaseous wastes, large quantities of solid wastes are also generated during leather processing and subsequently during effluent treatment (Germann, 1999). Although some of the wastes find limited applications, the safe disposal of the bulk of the solid wastes has posed serious problems. The types of solid wastes generated in a tannery processing 1 ton of raw skins/hides have been quantified in Table 2 (Kaul and Ravindranath, 1999).

III. COMBATTING ENVIRONMENTAL CHALLENGES: TECHNOLOGICAL MEASURES

Environmental challenges from leather processing arise from both the nature and the quantity of wastes discharged. In combatting the environmental challenges in the leather processing industry in general and in developing countries in particular, there has been an attempt to emphasize the role of effluent treatment plants (ETPs) (Rao et al., 1999). Conventional tannery ETPs

TABLE 2. Nature and Quantity of Solid Wastes Produced from Processing 1 Ton of Raw Skins/Hides

Nature of solid waste	Quantity (kg)
Salt from handshaking	80
Salt from solar pans (not realized)	220
Hair (pasting ovine)	100
Raw trimmings	40
Lime sludge (mostly bovine)	60
Fleshing	120
Wet blue trimmings (grain splits)	30
Chrome splitting (bovine)	65
Chrome shaving (mostly bovine)	95
Buffing dust (including shaving bovine after crust)	65
Dyed trimmings	35
Dry sludge from ETP	125

Note. From Rao et al. (2004).

offer physicochemical treatment followed by biological and tertiary treatment to meet the standards (Rao et al., 1999). Significant technological advancements are being made in the end-of-pipe treatment methods to achieve higher efficiency in meeting the standards in a cost-effective manner. The anaerobic treatment of tanning wastewaters in different locations in India has included the application of technologies based on lagoons, contact filter, upflow anaerobic sludge blanket (UASB) reactor, and high-rate biomethanation (van Groenestijn et al., 1995; Rajamani et al., 1995; Ramasami and Sahasranaman, 2000). Technologies based on biomethanation attempt to convert the organic wastes into methane. UASB technology for the treatment of tannery wastewaters is indeed relevant by virtue of the advantage of lower energy and area requirements. Although anaerobic treatment of tannery wastewater is efficient to reduce the BOD and COD loads by 50–60%, posttreatment using aeration methodologies is essential to achieve 30 ppm and 250 ppm BOD and COD norms (Buljan, 1996), respectively, in India and many other countries. Such posttreatment methodologies for tannery wastewaters from anaerobic biodigestion have included the use of aerators with and without the aid of aerobic microorganisms. A new method based on wet air oxidation at ambient pressure and temperature conditions has been developed and successfully commissioned in individual ETPs in India (Sekaran et al., 1999). A new posttreatment technology, chemoautotrophic activated carbon oxidation, developed and adopted for treating tannery wastewaters after anaerobic treatment and filtration, enables reduction of COD, sulfates, and color. Activated carbon filters, reed bed and root zone techniques, and reverse osmosis methods are being investigated for providing tertiary treatment of tannery wastewater (Rajagopalan and Thimmapuram, 1997; Daniels, 1995). The high-rate transpiration system has emerged as a possible method for treating salt-bearing tannery wastewaters (Rao et al., 2001). Recently, an accelerated evaporation and crystallization of saline streams using flat-plate collectors and sprinkler systems has been developed (Buljan et al., 2001).

Some of the technological options for the handling of solid wastes (Kaul and Ravindranath, 1999; Scheijgrond, 1998) are as follows. Timmings of raw hides/skins and pelts and fleshings can be utilized for glue manufacture. Collagen recovered from raw hide/skin and leather trimmings can be advantageously used in the preparation of collagen-based biomaterials for medical and other applications (Kumar et al., 2002; Sai et al., 1995; Balasubramani et al., 1997; Huc, 1985; Miller, 1996; Taylor et al., 1997, 1998). The salt obtained from mechanical desalting and solar evaporation can be used for curing or pickling or be disposed off in a nearby area. Biomethanation of fleshings and solid sludge from primary and secondary treatments is an economically viable option for secured disposal (Aloy et al., 1989). The hair recovered from leather processing is conventionally used for the manufacture of low-priced rugs and carpets. Keratin, a protein of hair, has also been converted into hydrolysate and used as a tanning aid (Ramamurthy et al., 1989). Sludge from lime pits finds use in land filling as well as in construction of low-priced houses. The barks and nuts from vegetable tanning can be used as fuel for boilers and brick kilns and as a soil conditioner (Parks, 1916; Herlihy and Billings, 1996). The shavings, trimmings, and buffings of vegetable- and chrome-tanned leather find usage in the manufacture of leather boards (Gish, 2000; Sykes, 1997b; Okamura and Shirai, 1972). It has also been shown that chrome shavings can be used as a reductant in the manufacture of BCS (Rao et al., 2002a). A new parchment-like material from chrome shavings has been developed and is found useful in the manufacture of home furnishing products (Rose et al., 2001).

The cost-effectiveness of waste treatment and management in the leather processing sector has long remained a most important issue. There is now an emerging recognition that the environmental issues in the leather processing sector are better managed by a new approach. The approach involves (a) pollution avoidance through waste minimization, (b) technological upgrading of waste treatment systems, and (c) safe disposal of treated effluent and sludge into receiving bodies with adequate precautions to avoid ecological destruction. The role and importance of technological measures to combat environmental challenges from leather processing activity are now increasingly recognized.

IV. WASTE MINIMIZATION IN LEATHER PROCESSING: A STEP FORWARD

The measures for waste minimization in leather processing involve a close audit of the type and quantity of chemicals used, exhaustion levels of chemicals used, amount of wastes generated, and possible technological and management steps needed to reduce wastes and ensure that the wastes discharged are treatable. Tannery waste management has become a matter of serious concern in recent years, and noncompliance with environmental regulations has resulted in closure of tanneries in some parts of India (Sykes, 1997a; Sahasranaman and Buljan; 2000). The assessment of the extent of pollution and identification of sources through a process audit has been carried out in different tanning centers in India to evolve effective and appropriate strategies for mitigating the pollution-related problems faced by the leather industry. These are essential if leather processing is to be rendered environmentally sustainable.

In-plant control measures for mitigating tannery pollution generally aim at the reduction or elimination of toxic wastes through process adjustments (Ramasami et al., 1994). It is generally believed that lasting solutions to the problem of tannery pollution rest in cleaner processing. The development and implementation of cleaner technologies in general require (a) careful auditing of the toxicological characteristic of every chemical inputs, (b) avoiding environmentally sensitive chemicals, (c) ensuring near total absorption of chemicals used, (d) assessing the environmental impact of the resulting process wastes, and (e) cost-benefit analysis and optimization of processes for best economic returns. The commonly used criteria for the selection of cleaner leather processing are (a) environmental impact of process wastes, (b) treatability of process wastes, (c) environmental quality of treated wastes, (d) costs of after-treatment and (e) optimization of process water.

V. CLEANER LEATHER PROCESSING: EMERGING TECHNOLOGICAL OPTIONS

Prevention or redution of pollution at the source through in-process control measures is assuming greater significance in the leather industry due to the realization that end-of-pipe treatment alone is not enough to meet the stringent specifications laid down for the discharge of treated wastewater by pollution control authorities. The strategy for in-process control for pollution reduction should attempt to integrate cleaner process options with efficient water management practices, as the volume of effluent has a direct influence on the cost of treatment of effluent (Parthasarathy, 1995). The reuse of spent liquor after the removal of the pollutants in suitable unit operations should be considered. The ideal strategy should be aimed at zero or near-zero discharge of waste liquors (Sykes, 1997a). The cleaner processing options recommended need to be cost-effective in order to be economically viable. Costing should take into consideration the cost of the treatment of effluents in the absence of such options. The success of cleaner technologies depends on the following factors: (a) reduction of pollution in terms of quantity and quality, (b) tanners' benefits in terms of leather quality improvement and/or cost reduction, (c) reproducibility of the process, (d) cost effectiveness to be economically viable, and (e) wide market opportunities.

A. Curing

One of the major sources of pollution from tannery wastewater has been identified to be common salt or sodium chloride (Sundar and Muralidharan, 1999). This emanates largely from the curing, pickling, and chrome tanning practices used in the leather processing. Saltless or less-salt curing as an alternative to wet salting presents an interesting technological option (Ludvik and Orlita, 1986). Some of the cleaner curing methods are (a) solar drying, (b) freeze drying (Stephens, 1987), (c) microwave/dielectric drying (Komanowsky, 2000), (d) use of KCl in place of NaCl (Bailey, 1995a), (e) borax–phenol (Selvarangan and Shanmugasundaram, 1984), (f) zinc chloride (Money, 1974), (g) silica gel and a low amount of salt (Kanagaraj et al., 2000) and (g) metal oxinates (Bailey et al., 1976; Barrett, 1986). Management options include processing green hides and skins, gamma (Bailey, 1999) and electron beam (Bailey et al., 2001; Bailey and Haas, 1988) irradiation techniques, and transportation in refrigerated trucks (Bailey, 1995b). Although saltless curing processes do exist, wet salting is the most commonly followed in commercial practice due to its low cost and high efficiency.

B. Desalting

Desalting of wet-salted raw stock prior to soaking forms an easy and implementable mode of reducing salt concentrations in tannery wastewater. Desalting can be done either manually or mechanically. Manual methods implicate dusting or brushing off the physically adhering crystalline salt. Through this method, it has been observed that nearly 30–40% of the total salt contained in wet salted skin or hide material can be removed (Rajamani and Viswanathan, 1998). Mechanical desalting is carried out by the drumming of wet-salted stock in a specially made slotted drum at 4–6 rpm. Air blowing or the use of small amounts of rinse water can further facilitate the process. Such desalting technologies also lead to better opening of fiber bundles and significant reduction of the carryover of salt into the subsequent streams like liming. Wheel-type desalting machines have been designed and used for efficient desalting of skins (Rao et al., 2001). The recovered salt can be reused for curing fresh hides/skins as well as in pickling processes. The benefits of desalting include (a) increase in the efficiency of soaking, (b) reducing the amount of carryover salt, thereby reducing the pollution load, and (c) recovery of salt.

C. Soaking

In-process control in soaking should aim at the reduction of TDS due to dissolved chloride as well as the volume of wastewater discharged. In total, salt alone accounts for 60–70% of the TDS in processing (Ramasami et al., 1999b). The waste soak stream is currently being segregated and taken for solar evaporation. Efforts should be made to eliminate salt as much as possible for a better management of the problem. Generally, the soaking processes adopted in commercial practices involve cocurrent flow of materials, namely, skins and hides on the one hand and soak liquor on the other (with 3 changes of water of 300% of raw weight). To reduce the discharge of waste soak liquor, a countercurrent soaking method has been found to be very effective. Countercurrent flow of materials could lead to a reduction in the amount of water used by nearly 50–60% in soaking operations (Rao et al., 2003). This offers an opportunity to reduce the hydraulic load by 20% in total volume of wastewater.

D. Green Fleshing

Green fleshing is advocated to reduce the consumption of chemicals on the one hand and to get more uniform results in liming on the other. In Western countries, efforts are made to remove the flesh as much as possible in the abattoir itself. By green fleshing, it has been possible to reduce the weight of the stock by nearly 10% (Langerwerf and Chandrababu, 1999).

E. Liming and Reliming

The conventional process uses lime and sulfide in high proportions (Money, 1996). Lime is a poorly soluble alkali, so there are advantages from limited availability of dissolved alkalis. There are also disadvantages in generation of a large quantity of solid wastes. Lime-free processes for the consolidation of leather-making substances and enabling the removal of flesh are now available, with limited success (Cantera et al., 1996). Although sulfide is toxic, it is the prime depilant in the unhairing process. Reduction of sulfide at the source is now possible using enzyme-assisted processes (Taylor et al., 1987). The cleaner options for liming include (a) the use of enzymes or other unhairing assists to reduce sulfide offer for a hair-saving liming process (Money and Scroggie, 1971; Heidemann and Smidek, 1987), (b) the possibility of recycling spent relime liquors for unhairing (Komanowsky and Senske, 1982; Money and Adminis, 1974), (c) completely replacing the hair pulping method of the unhairing process (Cantera, 1998; Feigel, 1998a), (d) effective methods of filtration to prevent the loosened hair from going into the effluent (Fadel and Speranza, 1995; Cranston et al., 1986a) and (e) the optimization of quantities of water used in pit or paddle liming.

Significant efforts have been made in the past five decades to render the dehairing process in tanneries cleaner. Sirolime (Cranston et al., 1986a, 1986b) and Darmstadt through-feed unhairing processes (Heidemann and Harenberg, 1972; Heidemann, 1993) are based on the conventional chemical inputs. The sirolime process consists of an impregnation stage with hydrosulfide and then a brief wash followed by oxidation of hydrosulfide external to the hide. Lime is then added and hair loosening occurs due to localized attack on the hair root by the sulfide ions generated within the hide. Hair is recovered by filtration and any residual hair is destroyed in a secondary liming stage by the addition of sulfide, additional lime, surfactant, and recycled lime liquor. A Darmstadt University group has introduced a continuous-flow unhairing technique. Fresh or well-soaked hides hung over the bars along the backbone hair side up are sprayed with 5–10% sodium sulfide solution in technical concentration in a cabin for 5–20 min. The hairs are transformed into a pulp and then stripped off with a special stripping cylinder device with plastic blades. These pelts are instantly fleshed and subsequently splitted.

Dimethylamine (Somerville et al., 1963; Hetzel et al., 1965, 1966), thioglycolic acid, sodium thioglycolate, and performic acid (Kamal et al., 1998; Uehara et al., 1986; Goddard and Michaelis, 1934; Fava et al., 1957) have been used to replace sulfide for dehairing. These, however, are not commercially successful for various reasons, such as cost, efficiency, and toxicity (von Vlimmeren, 1976). Rosenbusch (1965) reported the use of chlorine dioxide for dehairing. Morera et al. (1997) studied the use of hydrogen peroxide in alkaline medium for dehairing by an oxidative mechanism. However, the reduction in pollution load, especially COD, is not significant. Sehagal et al. (1996) developed a nonenzymatic, sulfide-free dehairing process using 1% nickel carbonate, 1% sodium hydroxide, 5% lime, and kaolin, along with water, through a painting technique. Disposal or recovery of nickel compounds, however, poses serious health problems. Schlosser et al. (1986) reported the use of *Lactobacillus*-based enzymes at acidic conditions for dehairing. This method leads to the solubilization of collagen at the experimental conditions. Valeika et al. (1997, 1998) found that the additons of salts such as sodium chloride, sodium sulfate, sodium formate, or sodium hydrogen phosphate influences the extent of hair removal, as well as opening the dermis structure.

Röhm (1910) developed the first successful enzymatic unhairing, the Arazym process, as described by Green (1952). Enzymatic unhairing (using enzymes, generally based on protease, along with small amounts of sulfide and lime applied as paint on the flesh side) causes loosening of hair by selective breakdown of cementing substances and presents a hair-saving approach (Green, 1952; Bose, 1955; Pilawski and Felicjaniak, 1976; Jones et al., 1968; Dhar, 1974; Puvanakrishnan and Dhar, 1986; Brady et al., 1990). Enzyme-assisted processes for the removal of hair are associated with both merits and demerits (Feigel, 1998b; Taylor et al., 1987). The demerits perceived are

(a) fear of possible damage of leather-making substances, (b) inadequate fiber opening, (c) flatter grain and substance, and (d) higher chemical costs. The recognized merits are (a) higher area recovery, (b) smoother grain, (c) better in-plant ecology, and (d) higher efficiency of wastewater treatment devices. There is a possibility to overcome the demerits through proper process optimization and control by using a combination of enzyme with sulfide (Technology Plan, 1997). An increase in the area of the final leather by 2–3% due to enzymatic unhairing has been demonstrated (Thanikaivelan et al., 2001a; Shrewsbury, 2002). It is now possible to use enzyme-assisted dehairing methods as alternatives to sulfide-based processes with benefits of reduced BOD, COD, TDS, and sulfide levels in wastewater, as well as improved efficiencies of wastewater treatment plants (Rao et al., 2001).

Lime-free fiber opening methodologies have scarcely been attempted. These include the use of strong alkalis (Herfeld and Schubert, 1969), *Lactobacillus*-based enzymes (Schlosser et al., 1986), lyotropic agents (salts/acids that cause lyotropic swelling), and bating enzymes (Thanikaivelan et al., 2001a). These methodologies, however, have limited applications due to improper opening of fiber bundles.

Lime splitting for heavier hides would considerably reduce the cost of chemicals used, apart from reducing the water consumed in processing. There is also the possibility of a reduction in processing time. Area yield has also been found to increase by about 5% when lime splitting is done (Borge, 1986; Mance, 2000; Langerwerf and Chandrababu, 1999). Although Indian cow hides are not thick enough for lime splitting, this method would be tremendously useful for buffalo and imported hides. The washings of limed pelts can be reused for liming. This would considerably reduce the pollution load as well as the volume of wastewater discharged.

F. Deliming

The use of ammonium chloride and ammonium sulfate adversely affects the characteristics of the effluent (Huber and Satyendra, 1990). They contribute to 75–80% of the ammonia in the effluent. Although the ammonium salts are cheap and perform efficiently, the increase in COD of the wastewater generated in the operation, apart from the generation of dissolved ammonia–nitrogen, gives rise to difficulty in effluent treatment. The ammonium sulfate, which is prevalently used, also contributes to dissolved sulfate. Hence, alternatives are sought to reduce the pollution load. These alternatives are based on organic and inorganic acids, esters of carboxylic acids, and nonswelling aromatic acids (Streicher, 1987; Frendrup, 1996). The costs of these products are prohibitively high when compared to ammonium salts and hence they are yet to be commercially exploited. Ammonia-free deliming has gained importance in many countries. Carbon dioxide deliming has been carried out in some cases with success (Munz and Toifl, 1992; Purushotham et al., 1993). In these instances, environmental as well as other quality benefits have been reported. The issues needing special process adjustments include (a) complete removal of sulfide prior to deliming, (b) the need for acid rather than conventional alkaline bate, and (c) rigorous process control systems.

G. Pickling

The pickling process contributes to TDS in the form of chlorides considerably, and this is not amenable to treatment via currently used end-of-pipe treatment methods. As mentioned earlier, the current management practice involves the solar evaporation of this stream mixed with the soak liquors. The long-range solutions should include the possibility of saltless pickling (Pojer and Huynh, 1999) and pickleless chrome tanning options (Dasgupta, 1998). The immediate solution would be to consider the pickle recycle options (Burrows, 2001), which would considerably reduce the load in solar evaporation, which becomes the bottleneck in increasing the capacity of production. The concept of using nonswelling acid in pickling is already known, but this has not been commercially exploited due to the high cost involved (Pojer and Huynh, 1999; Rao et al., 2002c). There are many commercial products available based on naphthalene sulfonic acids, sulfonated aromatic dicarboxylic acid like phthalic acids, and auxiliary agents (Palop and Marsal, 2002; Post, 1964; Herfeld and Schubert; 1975). The latter class of compounds is quite interesting because they also help in improving the exhaustion of chrome and hence the increase in the cost can to some extent be justified.

The commercial practice is to retain 50% of the pickle float for tanning (Sundar et al., 2002). The remaining 50% is currently taken for solar evaporation. There exists a possibility of reusing this pickle liquor after the removal of the fibrous materials safely through filtration, for the next batch after replenishment with salt and water (Burrows, 2001). Such recycle and reuse methods reduce TDS of the effluent discharged from the identified stream.

H. Chrome Tanning

Among the various tanning systems, mineral tanning in general, and chrome tanning in particular, have been popularly followed in commercial practices due to aforementioned reasons. Much of the efforts for pollution reduction are mainly focused on chrome tanning because chromium is considered to be toxic (Leonard and Lauwerys, 1980; Katz, 1991; Dartsch et al., 1998). The biotoxicity of chromium has been a subject of active discussion. Although the implication of chromium(III) in glucose and lipid metabolism has been considered beneficial (Govindaraju et al., 1989; Anderson et al., 1997; Mertz, 1998), epidemiological and animal studies have firmly established hexavalent chromium compounds as potent carcinogens (Costa, 1991). Once inside the cell, Cr(VI) is reduced to lower oxidation states (V, IV, and III) (Arslan et al., 1987). Cr(III) species have been shown to be mutagenic and genotoxic (Jennette, 1979). Although trivalent chromium compounds are kinetically inert to ligand substitution reactions, they do react strongly with DNA and proteins (Balamurugan et al., 1999). Trivalent chromium leads to the formation of different Cr–DNA adducts such as DNA–protein, interstrand DNA, and DNA–amino acids cross-links (Wedrychowski et al., 1985; Zhitokovich et al., 1995, 2000). Some of the Cr(III) complexes containing aromatic imine ligands have been found to be mutagenic in *Salmonella typhimurium* (Beyersmann and Koster, 1987). Salen-based Cr(III) complexes have been found to induce apoptosis in lymphocyte cell cultures (Rajaram et al., 1995). Some of the Cr(III) complexes in specific ligand environments have been proposed to bring about oxidative damage to plasma proteins, glycoproteins, and DNA (Shrivastava and Nair, 2000, 2001; Tsou et al., 1997; Voitkun et al., 1998; Vijayalakshmi et al., 2000). Effects of soil pollution by the metal ion are observed when soil contains large amount of soluble and biologically assimilable forms of chromium (Bartlett, 1991). A part of Cr(VI) present in the soil may be reduced by soil reductants (Bartlett and Kimble, 1976). When soluble Cr(III) is added to soil, manganese oxides present in the soil may cause oxidation to Cr(VI) (Bartlett and James, 1979). Cr(VI) is shown to be 500 times more toxic than Cr(III) (Venier et al., 1982).

Conventional chrome tanning salts and methods give an uptake of only 40–70% of the material used during tanning, resulting in the wastage of material on one hand and ecological concerns on the other (Gauglhofer, 1986; Prasad et al., 1987; Ramasami, 1996). The value of this loss is approximately US$10,000,000 per annum in India (Ramasami, 1996). The treatment of chrome-bearing wastes through normal physicochemical methods results in chrome-bearing sludge, whose disposal is a serious problem (Warrier et al., 1995a, 1995b).

1. HIGH EXHAUST TANNING

It is now technologically possible to increase the absorption of chromium during chrome tanning to above 85%. There are commercial external aids (Luck, 1980; Chandrasekaran, 1987), intrinsically modified chrome tanning salts (Rao et al., 1998; Suresh et al., 2001; Thanikaivelan et al., 2002a) with high exhaustion level, and chrome tanning systems with more rational pickling and tanning (Rao et al., 1992), which ensure higher absorption of chromium. The preparation of high-exhaust chrome tanning salt has become technically feasible through designed alterations in the process of manufacture of the chrome tanning salts, wherein the formation of low-affinity species has been avoided to increase the absorption levels (Rao et al., 1998). Most high-exhaustion methods discharge wastewater from sectional chrome tanning streams with chromium concentrations on the order of 300–750 ppm.

These streams are not directly amenable for discharge. While economic advantages of the high exhaustion chrome tanning are evident, further processing of waste streams of the chrome tanning yard needs to be integrated.

2. DIRECT RECYCLING

Extensive studies have been made on the use of spent chrome liquor as a pickling or tanning bath (Davis and Scroggie, 1973, 1980; France, 1975; Rao et al., 2002c). Direct recycling of spent chrome tanning liquors for pickling causes surface fixation of chromium due to high chromium concentrations. Also, direct recycling of chrome liquors increases the concentration of neutral salts, which reduce the chrome uptake in subsequent batches. Direct recycling of spent chrome liquor after preacidification to a pH around 1.0 results in leathers without any surface deposition of chromium (Davis and Scroggie, 1980). A system based on membrane separation for the selective removal of chromium from neutral salts has been developed (Rao et al., 1989). This system makes use of a chrome-rich stream for tanning and a neutral-salt-rich stream for pickling. The economic viability of the technique is yet to be established.

3. CLOSED PICKLE–TAN LOOP

High-exhaustion methods ensuring absorption of 85% of chromium are still not environmentally acceptable. A typical method based on Alutan (an aluminum syntan)–BCS for tanning has been developed (Rao et al., 2002c; Chandrababu et al., 1995; Ramasami et al., 1999a). The exhaustion levels of chromium and aluminum exceed 90%. The spent solution is recycled as pickle floats for subsequent batches instead of being discharged, thus generating a closed loop with zero discharge of chromium. The highlight of the system is an overall saving of US$30–40 per ton of leather processed. The system also ensures reductions in BOD, COD, and TDS loads on ETPs, as well as saving water.

4. CHROME RECOVERY AND REUSE

Chromium in the sectional streams of wastewater can be recovered, regenerated, and reused effectively through a chrome recovery/reuse methodology (Rao, 1987; Covington et al., 1983). In this method, chromium is precipitated with an alkali as chromic hydroxide, allowed to settle under gravity, separated from the supernatant, and redissolved in sulfuric acid (Sreeram et al., 1999). The recovered chrome is reused as a tanning salt in the admixture with fresh BCS after replenishment (Prasad and Nair, 1994; Venba et al., 1999). Chrome recovery/reuse plants have already established commercial viability. The process is simple and easy to adopt. It is financially attractive as the payback period is 1–2 years for a plant of 5–10 m^3 capacities (Rao et al., 1995; Langerwerf, 1999). A semicontinuous chromium recovery process for large volumes of wastewater has been developed for commercialization

(Sreeram et al., 2000a). One such plant has been installed in Tamil Nadu, India, at a capacity of 24 m^3. Because the chrome recovery process ensures that the sectional wastewater from the chrome tanning operation is segregated and handled, sulfate-bearing streams can be diverted away from the biomethanation reactors (Rajamani et al., 1995). This would facilitate a greater efficiency of biomethanation. The TDS problem, however, needs to be addressed separately even when a chrome recovery/reuse process is adopted.

Attempts have been made to recover chrome as high-purity chromium from tannery effluents (Deep et al., 2001). A three-step process involving precipitation, extraction, and electrodeposition has been developed by Gupta et al. (2002) for the recovery of chromium(III) from tannery effluent. A solvent extraction technique for recovering chromium from spent chrome liquor has been developed using Cyanex 301–toluene (Khwaja et al., 2000a) as well as mono(2-ethylhexyl) phosphoric acid–*n*-hexane (Khwaja et al., 2000b) systems. Recently, an attempt has been made to remove chromium from tannery effluent using seaweed, *Sargassum* species, and to reuse the chromium-bearing seaweed in the manufacture of BCS as a reductant (Aravindhan et al., 2004a).

5. TWO-STAGE CHROME TANNING

A new two-stage chrome tanning system has been evolved to overcome the environmental problems of chrome tanning (Muralidharan et al., 2001). In this system, the pickled pelt is treated with 10% (w/w) BCS (on fleshed weight of hides and skins) initially with a sufficient quantity of water. After ensuring complete penetration of chromium in the skin matrix, the spent chrome solution is drained before the basification process and reused in the place of chrome tanning salt for subsequent batch. The chromium-treated skin matrix is subjected to basification subsequently. The spent liquor from this process contains a low concentration of chromium and hence is reused for the preparation of pickle liquor for the next batch, for efficient management of chromium.

6. PICKLELESS CHROME TANNING

Pickleless chrome tanning is a recently introduced concept (Venba et al., 1995; Dasgupta, 1998) to not only do away with the use of salt (sodium chloride) in tanning but also increase the exhaustion of chrome and considerably reduce the salt generated in basification on account of the very low pH associated with the conventional pickling prior to chrome tanning. It is theoretically estimated that the reactivity of chrome can be enhanced by increasing the starting pH from 2.8 to 5.5 (Covington, 1986). To start the chrome tanning at such an elevated pH, one has to make sure that there is no problem with either penetration or distribution of chrome in the fibre matrix. Recently, a method based on pretreatment with ethanolamine–formic acid has been standardized, and its effect on the quality of leather has been studied

(Prentiss and Prasad, 1981; Chandrababu et al., 1995; Covington, 1997a, 1997b; Thanikaivelan et al., 2001a). By using this method, it is possible to get a more uniform distribution of chrome even if the pickling pH is not uniform throughout the cross section. Earlier reports, however, suffer from the use of some specialty chemicals such as carbon dioxide (Munz et al., 1997), chrome syntan (Suresh et al., 2001), modified BCS (Thanikaivelan et al., 2002a), or a small amount of sodium chloride (Munz et al., 1997). Tanners around the world are reluctant to use this method due to fear of grain swelling and surface precipitation, although no evidence of these problems has been shown to date.

7. LESSCHROME AND CHROMELESS TANNING TECHNOLOGIES

A chromium–iron tanning agent as a chrome-saver approach has been developed (Thanikaivelan et al., 2000a). In a select ligand environment, the negative attributes of iron tanning such as deterioration and darkening of color on aging were avoided. The leather made from this tanning agent exhibits a shrinkage temperature of about 115°C and meets all the required chemical and physical properties. Natural colors based on Cr–Fe tanned leather by treating with vegetable tanning materials have also been developed (Rao et al., 2002b). Chromium–silica-, aluminum–zinc-, chromium–zinc-, chromium–zinc–silica-, and aluminum–tannic acid–silica-based tanning agents have been developed (Thanikaivelan et al., 2000; Madhan et al., 2001a, 2002; Fathima et al., 2003, 2004) for reducing the chromium emission and improving the physical and bulk properties of the leathers.

The use of alternative mineral tanning salts has been proposed and attempted with varying degrees of success (Chakravorthy and Nursten, 1958). Aluminum has been considered as an alternative to chromium for many years (Selvarangan and Nayudamma, 1964; Montgomery, 1987; Takenouchi et al., 1997; Taqui-Khan, 1987). The majority of commercially adopted aluminum-based tanning salts suffer from some limitations. Particularly, the fatliquoring and retanning systems require substantial modification. This in part is because of the high cationic potential of aluminum salts. It has been possible to develop a suitable alternative approach to reduce the cationic potential and render Al(III) with transition-metal-like behavior (Kanthimathi et al., 2002). This has been possible because of insight into the aqueous chemistry of Al(III) salts.

Zirconium(IV)-based tanning systems have remained an attractive possibility but suffer from disadvantages associated with low pH values required to avoid insolubility of the tanning salts (Ranganathan and Reed, 1958). Through manipulation of acid–base behavior of the coordinated water ligands by influencing the ligand environment, it has been possible to raise the pH of precipitation to values as high as 4.0 (Sreeram et al., 2000b). The use of zirconium oxychloride in a select ligand environment as a solo tanning agent has been demonstrated (Sundararajan et al., 2003; Madhan et al., 2003). These systems, if made costeffective, can emerge as chrome savers. Titanium-based tanning salts and mixtures of metal oxides as combination tanning systems have been developed (Covington et al., 1998; Covington, 1998; Tate, 1989). Some of these salts are being commercially used to a limited extent.

Organic tanning. It has now been possible to avoid completely the use of mineral tanning salts in the manufacture of soft types of leather including suede garments (Covington and Shi, 1998). It is also possible to process richly dyed garment suedes based on vegeable and some organic tanning adjuncts (Madhan et al., 2001b). In these processes, the role and importance of surface charges assume much significance. The underlying process chemistry is becoming well understood. These technological options open up new avenues for ecofriendly tanning methodologies (Covington, 1998).

I. Posttanning and Finishing

Posttanning operations involve the use of retanning agents, fatliquors, dyes, and finishing chemicals. Exhaustion levels of many of these materials have not been quantitatively assessed. Treatability of posttanning chemicals and the neutral salt content form two important criteria that need closer scrutiny. Contributions to COD from many retanning agents and fatliquors are significant. This can be mitigated by the use of optimized quantities of high-performing chemicals, which would lead to less discharge of biotreatable residues.

The various in-process control options for cleaner wet finishing are as follows (Langerwerf and Chandrababu, 1999):

- Screening of retanning and fatliquoring agents for selection, based on their biodegradability and uptake behavior.
- Retanning materials based on amino resins and other compounds that are capable of contributing to BOD and COD should be avoided as far as possible.
- Fatliquors based on chlorinated paraffins should be avoided; there is a concern regarding absorbable organic halides in many countries (Cuq and Delmas, 1999).
- Benzidine and other arylamine based azo dyes, which are potentially carcinogenic, should be totally eliminated (Turner, 1994; Püntener, 1998).
- Dyes should be screened for their exhaustion characteristics, and only high-performing dyes should be used (Page and Fennen, 1998).
- Rationalization of the entire wet finishing operations is needed in order to optimize the quantities of various chemicals used, thereby reducing the discharge of chemicals in waste streams.

Optimization of such chemical inputs as well as the choice of inputs based on treatability data form the most practical mitigation strategy. Such data have now been compiled for a series of chemical formulations (Technology Plan, 1997). Aqueous finishing formulations (Wenzel, 1991; Pulles, 1990), formaldehyde-free finishing (Gill, 1995; Wu-Sheng et al., 2000), the audit of azo dyes for environmental acceptability (Püntener, 1998), and biodegradable biocides (Hauber, 1998) have attracted interest.

Pollution reduction in finishing-yard effluent would involve the following measures (Grif, 1990):

- Minimizing the wastage and emission by proper control of spraying machines (Stockman, 1988; Mannouch, 2002).
- Use of new application methodologies such as roller coaters or low-pressure spray pistols (Will, 1985; Biles et al., 1985; Pulles and Domanjko, 1985; Löbig, 1997).
- Elimination of lead and other toxic-metal-based pigment formulations (Hay, 1979).
- Minimizing volatile organic compounds by resorting to water-based formulations, especially in finishing (Gill, 1991, 1993; Walther, 1988; Cluthe et al., 1978; Biles 1990; Lach et al., 1988; Hanson, 1982).
- Use of newer and safer cross-links in protein finish in place of formaldehyde (Gill, 1995).

VI. NOVEL CONCEPTS IN LEATHER PROCESSING: APPROACHING ZERO-DISCHARGE TANNING

Leather processing activity involves the use of several chemicals, some of which are not utilized completely (Ramasami et al., 1999b). Excessive use and poor uptake of chemicals form inevitable sources of pollution. Some of the chemicals used are inherently constrained with respect to their environmental consequences. To wipe out the negative image the activity has created for itself and to move toward sustainable development, it now seems more appropriate for the global leather sector to implement cleaner process options to reduce the environmental risks from the sector. A closer audit of various operations would provide not only the origin of current ecological constraints from the leather industry but also clues to resolve them. The environmental protection authorities have specified discharge norms based on carrying capacity and societal needs. Although end-of-pipe treatment technologies for achieving wastewater discharge norms do exist, real solution lies in approaching zero discharge of pollutants (Pauli, 1997; McCleskey et al., 2001).

There is a need to revisit the leather making operation anew. The wide variations in pH of the skin matrix during the various steps in leather making are bound to impair the bulk as well as surface properties, apart from contributing to the generation and discharge of neutral salts. An appropriate approach would be to render the tanning activities cleaner through near-zero discharge of pollutants. This approach would target the development of leather processing methods limiting the pH profile needed for various operations to a narrow range. The net benefits from such an approach will be

- Reduction in the use of chemicals.
- Reduction in cost.
- Reduction in utilities such as water and power.
- Rationalization of processes.
- Elimination of several processes, namely; liming, reliming, deliming, and pickling.
- Reduction in process time.
- Reduction in TDS in tannery wastewaters.
- Reduction in sludge volume, especially the total removal of lime sludge.
- Higher utilization of materials like chromium.

Ideally, zero discharge of wastewater is most desirable. As a practical measure, however, reduction of the discharge of water to 5–6 L/kg leather will be a good initial step. Approaching the zero-discharge value is an intellectual as well as a global challenge. This would need to consider and compare several strategies that are possible to avoid pollution. The approach demands the use of following concepts either alone or in combination:

- Usage of chemicals having low toxicity or less environmental impact.
- Near 100% utilization of chemicals.
- Recovery of water and valuable chemical inputs from each sectional stream of wastes and reuse in leather processing to the extent possible.
- Process innovation.
- Product innovation.
- Integration of processes.

Leather processing generally involves a combination of single- and multistep processes that use as well as expel various biological, organic, and inorganic materials (Germann, 1999). Hence, a strategy that involves combined advantages of all possible approaches would be ideal. This implies that the study of suitable zero discharge approaches for every single unit process is important. Studies on the soaking process are not attempted due to (a) the diverse nature of curing techniques, (b) availability of several in-plant control and salt recovery techniques, and (c) the real solution being in designing an ambient preservation technique. It is now possible to process green hides without loss in quality (Taeger, 1996). Hence, it has been proposed to redesign the pretanning and tanning processes excluding soaking by limiting the working pH to the range of 4.0–8.5. To achieve this, liming and reliming processes need to be redesigned such that the cross-section pH of the pelt (pH within the pelt) is 8.0. This implies that the deliming operation could be eliminated. The chrome tanning step needs to be designed without pickling and basification processes. Finally, the developed processes have to be integrated in order to achieve zero discharge of pollutants.

Proposed new research fields are as follows:

- Standardization of conventional liming and reliming chemical inputs and unearthing the role of concentration.
- Countering the problem of sulfide and lime sludge through bioprocessing:
  - Lime-free enzyme assisted dehairing.
  - Enzyme-based fiber opening by targeting the proteoglycans (protein conjugated with carbohydrates) present in skin/hide.
- Sodium hydroxide-based fiber opening to eliminate the problem of lime sludge.
- Design and development of a pickle and basification-free chrome tanning.
- Integration of best practices from dehairing, fiber opening and pickle-basification-free chrome tanning processes.

A. Some Early Results

1. ENZYME-ASSISTED DEHAIRING FOR COWHIDES

An enzyme-assisted dehairing process using sodium sulfide in an amount 85% less than that used in the conventional lime sulfide dehairing process has been developed (Thanikaivelan et al., 2000c). The process does not require lime for dehairing, thereby ensuring not only 100% elimination of lime sludge formation, but also complete removal of hair at an unusual pH (8.0). The pelts, however, require a reliming process, which in turn creates lime sludge and TDS problems.

2. NONLIME FIBER OPENING

A nonlime fiber opening method based on sodium hydroxide has been developed by Thanikaivelan et al. (2001b). An optimum concentration [1.0% (w/w) offer with 350% (v/w) water, based on weight of the dehaired hide] of sodium hydroxide has been established for optimal opening of fiber bundles. This has been substantiated through scanning electron microscopy, spent alkali liquor and pelt analysis, softness measurements, and stratigraphic chrome distribution analysis. The pelt analysis shows that the opening of fiber bundles has attained equilibrium, and the pH of the cross section is 8.5. Performance of the leathers is shown to be on par with conventionally treated leathers through physical and hand evaluation. Softness of the leathers is numerically proven to be comparable with that of control leather treated with lime. The process also enjoys elimination of the deliming process coupled with a 45% reduction in total solids (TS) load on the environment.

3. REDUCED FLOAT APPROACH

In an attempt to combat the pollution from beam-house processes, an ecofriendly way of doing the conventional liming–reliming processes has been found (Thanikaivelan et al., 2003a) by applying the beam-house chemicals optimally. This is based on the fact that swelling requires only 20 to 40% water (based on raw skin weight before soaking) for conventional fiber opening. This would, in principle, make possible the use of only one-tenth of the chemicals conventionally used in liming–reliming processes, maintaining the same concentration gradient. The process uses 40% (v/w) water, 0.35% (w/w) sodium sulfide, and 1% (w/w) lime for liming, and 40% (v/w) water and 1% (w/w) lime (percentages based on wet weight of skins after soaking) for reliming, with conventional process time of 1 day for each process, in a drum that runs intermittently. It has been found that the dehairing is complete and the extent of opening of fiber bundles is comparable to that of the control. This has been demonstrated through scanning electron microscopy, stratigraphic chrome distribution analysis, and softness measurements. Performance of the leathers is shown to be on a par with conventionally opened up leathers by means of physical and hand evaluation. Softness of the leathers is proven to be numerically comparable with that of conventionally treated leathers. The process enjoys reduction in COD and TS loads on the environment by 85% and 12%, respectively, compared to the conventional process. The total dry sludge from the liming–reliming processes is brought down from 152 kg to 6 kg for processing 1 ton of raw skins, which has been demonstrated for the first time.

4. LEATHER PROCESSING IN NARROW pH PROFILE

A leather processing technique for tanning skins/hides without deliming and pickling processes, in a narrow pH range, has been established (Thanikaivelan et al., 2001a). The process envisions the use of lyotropic agents for fiber opening and uses a pickleless chrome tanning system in a narrow pH range (4.0–8.0). Thereby, the process claims an environmental benefit of reducing the COD and TS loads by 67% and 64%, respectively. The developed process claims substantial reduction in water and time requirements as well.

5. BIOCATALYTIC FIBER OPENING: PARADIGM SHIFT FROM CHEMICAL TO BIOPROCESSING

In an attempt to combat the pollution from beam-house processes, an enzyme-based fiber opening process has been established (Thanikaivelan et al., 2002b). An approach has been made to do the beam-house processes using bioproducts. This is based on the fact that the enzymes specifically act on the substrate. Suitable enzymes have been designed in order to target hair and cementing substances, separately. The approach leads to paradigm shift from chemical processing to bioprocessing. It has been found that the dehairing is complete and the extent of opening of fibre bundles is comparable to leathers treated with lime. Scanning electron microscopy, stratigraphic chrome distribution analysis, and softness measurements confirm these findings. Quality of the leathers is shown to be on a par with conventionally opened leathers through physical and bulk property evaluation. Quantitative measurement of softness reveals that enzyme treatment provides softness for the experimental leathers numerically comparable to that of conventional lime-treated leathers. The total dry sludge from the liming–reliming processes is brought down from 152 kg to 12 kg for processing 1 ton of raw skins, due to the replacement of lime with enzymes. The amylase-treated hides, however, are further processed conventionally, soaking them first in a pickle bath consisting of a huge amount of salt and sulfuric acid and then chemically preventing them from rotting by treating with chrome tanning salt. This results in a significant increase of dissolved solids as well as chromium in the wastewater.

6. THREE-STEP TANNING TECHNIQUE: A MODEL FOR PROCESS INTEGRATION

The tailored pretanning process evolved in the earlier studies provides a clean collagen matrix having neutral pH. This provdes a clue on how to tan the skins directly without deliming and pickling (acidification), if one has an effective tanning system without a preacidification process. Recently, a chrome tanning system without a pickling process for conventionally limed and delimed collagen matrix has been developed (Legesse et al., 2002; Thanikaivelan et al., 2004a). Now it is possible to integrate the biodriven process with a pickle-free chrome tanning process (Thanikaivelan et al., 2004b). This results in complete revamping of the conventional leather process sequence. Generally, conventional tanning process involves “do–undo” processes like curing (dehydration)–soaking (rehydration), liming (swelling)–deliming (deswelling), pickling (acidification)–depickling (basification). Further wide variation in pH has been limited to a very short pH profile. The net benefits of this approach are countless.

It has been now shown that this enzyme-driven three-step tanning process is applicable not only to thin skins (Saravanabhavan et al., 2003a, 2003b; Aravindhan et al., 2004b) but also to heavy and thick hides (Thanikaivelan et al., 2003b, 2004c). The processed leathers show physical and tactile properties similar or comparable to those of conventionally processed leathers. The cross-section view of tanned cowhides through a scanning electron microscopy shows that the fiber bundles are not modified due to the change in a multistep process to an enzyme-driven three step tanning process. It has also been demonstrated that the biodriven three-step tanning is economically viable and attractive, if commercial enzyme products are used. Enzymatic processing when synergized with compact chrome tanning results in reduction of COD, TS, and chromium emissions into the environment by 80%, 85%, and 80%, respectively, compared to traditional processing. It cuts the amount of solid sludge that dehairing and fiber opening generate by 91%. It is also interesting to note that the enzyme treatment softens the matrix, thereby increasing the area of the final leather. This results in nearly US$100 savings for processing 1 ton skins/hides, because leather is sold on an area basis. Recently, there is also an approach to use plant-based polyphenol compounds for tanning instead of chromium at pH 8.0 (Saravanabhavan et al., 2004a) in the three-step tanning process (Saravanabhavan et al., 2004b).

VII. SUMMARY AND CONCLUSIONS

Leather processing involves cleaning of the skins or hides to remove unwanted materials, followed by preparing the stock for chrome tanning and subsequently tanning using BCS to stabilize the raw material against microbial degradation. The conventional cleaning processes (liming–reliming processes) lead to the generation of substantial amounts of sulfide, lime sludge, and BOD. The conventional preparatory process for chrome tanning, namely, pickling, which involves the use of sodium chloride and sulfuric acid, generates more amounts of dissolved solids. The chrome tanning process by virtue of its poor exhaustion behavior emanates liquor containing chromium at levels 1000-fold higher than the norm specified by pollution control authorities.

A critical review on the conventional leather processes and the principles behind each steps reveals that the bulk of the pollution rests in pretanning and tanning processes. Nevertheless, posttanning and finishing steps do pollute the environment by way of effluent as well as volatile organic compounds air emissions. State-of-the art technologies comprising both in-plant and end-of-pipe treatment solutions have been reviewed for their technical suitability and commercial feasibility. It turned out that a combination of both technologies is essential for protecting the leather industry from environmental consequences. The sustainability of the leather industry, however, relies solely on revamping the leather process sequence, avoiding do–undo methodologies based on first principles. An account of such developments has been catalogued and their technical features and practicability have been reviewed. Preliminary results show that the process schemes are capable of lowering environmental threats drastically. Further studies and commercial follow-up, however, would validate the developments.

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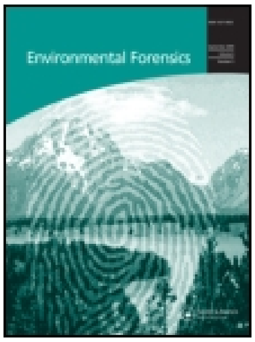

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MINI-REVIEW

The chlor-alkali process: A review of history and pollution

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ABSTRACT
The chlor-alkali process is a widely used electrolytic process that yields chlorine and caustic soda. It has been in use since the 19th century and is a primary industry in the United States, Western Europe, and Japan. There are three primary electrolytic processes for producing chlorine and caustic soda: the diaphragm cell process, the mercury cell process, and the membrane cell process. The first two have been used for over 100 years; the latter was developed in the past 60. The two oldest methods are used the most throughout the world and have been proven to be the most environmentally unfriendly through their use of asbestos and mercury, respectively. The membrane cell process is a superior method in its energy efficiency and lack of harmful chemicals. This article reviews the history of each method, addresses changes in its modern technology and use, and discusses the emissions and outputs of the processes.

KEYWORDS
Asbestos; caustic soda; chlor-alkali; chlorine; electrolytic; mercury

Introduction

The production and manufacturing of chlorine as a single element is an industry with a long history. This history reveals an ongoing evolution of technology and efficiency. The chlor-alkali process produces chlorine, hydrogen, and sodium hydroxide solution (U. S. Environmental Protection Agency [US EPA], 1995). The primary marketable products are chlorine and sodium hydroxide, also known as caustic soda. These substances are used throughout a myriad of different industries including construction, textiles, paper, and cleaning. Currently there are three different electrolytic processes used to produce chlorine: the diaphragm cell, the mercury cell, and the membrane cell (US EPA, 1995). All three produce chlorine and sodium hydroxide, but some are more efficient and produce less environmentally hazardous waste. The diaphragm and mercury cell processes are the oldest of the three; both were created in the late 19th century, the Griesheim diaphragm cell in 1888 and the Castner-Kellner mercury cell in 1892 (O'Brien and Bommaraju, 2005). These are also the two most widely used processes throughout the world.

The membrane cell process was developed in the 1950s and is slowly becoming a competitive alternative (O'Brien and Bommaraju, 2005). It has proven to be a more efficient, productive, and environmentally conscious method of electrolytic production of chlorine (European Commission, 2000). In 1989 in U.S., 94% of chlorine was produced by diaphragm or mercury cell processes (US EPA, 1995). Both of these processes use very toxic materials, asbestos and mercury, which cause irreversible damage to workers as well as the environment when waste is produced, which is inevitable. According to a report by the European Commission Joint Research Centre (1995), "The chlorine production of a country is an indicator of the state of development of its chemical industry." This means that the rate at which a nation produces chlorine is a sign of how much chemical work is done in that nation. The two top producers of chlorine are Western Europe and the U.S., both of which use diaphragm and mercury cell processes; Japan is the next largest producer, and the only country to produce chlorine primarily through the membrane cell process and to be totally mercury free (O'Brien and Bommaraju, 2005). The European Union has recently ruled that its chlor-alkali industry will be mercury free by December 11, 2017 (McCoy, 2015). In June 2000, 55% of Western Europe's chlor-alkali plants used the mercury cell process (European Commission, 2000). Now, only 23% of Europe in its entirety uses the mercury cell process, with only a year left to make the necessary changes required by

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the new legislation (Euro Chlor, 2015). This article will address the long history of innovation and inefficiency within a chemical industry that is slowly making efforts to transition to more environmentally friendly and energy-efficient methods, as well as examine the chlor-alkali process as a whole.

Diaphragm cell process

In the latter part of the 19th century chlorine was used primarily for the textile and paper industries. Chlorine was produced through the combination of manganese dioxide with hydrochloric acid:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O \text{ (at 100–110°C)} \quad (1)$$

Then advances were made and chlorine was produced from direct catalytic oxidation of hydrochloric acid with air:

$$4HCl + O_2(\text{air}) \rightarrow 2Cl_2 + 2H_2O \text{ (in the presence of CuCl catalyst at 450 – 460°C)} \quad (2)$$

This process was used for some time before it was discovered that steel, an iron alloy, is resistant to attack by dry chlorine. This discovery allowed the first commercial manufacturing and distribution of dry liquid chlorine in 1888 in Germany (O'Brien and Bommaraju, 2005). The formulas and science used for obtaining dry liquid chlorine in 1888 are still used in the diaphragm cell process today. As older methods of obtaining caustic soda were phased out, it also became necessary to find alternative ways to acquire chlorine. The electrolysis of brine to form chlorine was originally credited to Cruikshank in 1800, but in 1833 Faraday authored his laws of aqueous solutions, and not too long after, patents were issued to multiple people for the electrolytic production of chlorine from brine (O'Brien and Bommaraju, 2005). During the electrolysis process of NaCl, brine chlorine is separated at the cathode, and sodium hydroxide is produced at the anode (O'Brien and Bommaraju, 2005):

Oxidation at the anode:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad (3)$$

Reduction at the cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (4)$$

The net ionic equation:

$$2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + Cl_2(g) + H_2(g) \quad (5)$$

The "molecular" equation:

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g) \quad (6)$$

This would be applied to the creation of the diaphragm cell process, which was created in 1851, in order to keep the products, chlorine and sodium hydroxide, from coming back together after being separated and forming sodium hypochlorite. A British scientist, Charles Watt, discovered a way to separate the two products, and keep them separated throughout the reaction, with a current permeable separator. This allowed the current to pass through but kept the cathode and anode products separate (O'Brien and Bommaraju, 2005). This was a groundbreaking invention that made the commercial production of chlorine a feasible procedure. As time progressed, researchers in nations across Europe began inventing their own variations of the diaphragm cell process that Watt had introduced. The first commercially used cell for chlorine production was invented in 1888 in Germany by the Griesheim Company. The current permeable separator was made of porous cement and brine acidified with hydrochloric acid. Inventers in Great Britain also created their own diaphragm cell, as well as those in France and the U.S., and each cell had a variation from the original. Great Britain's Hargreaves–Bird cell was notable for its integration of asbestos into the construction and its vertical diaphragm cell. The U.S.-developed cell, the LeSueur cell, was groundbreaking in that it used a percolating diaphragm cell (O'Brien and Bommaraju, 2005). This is still the basis of chlor-alkali technology today because it allowed for a much higher efficiency than all of the previous methods.

As the 1900s moved forward so did innovation and invention in the diaphragm cell method. This brought more control over the process. Brine could be slowly fed into the system to prevent overflow. In the 1920s asbestos became a major part of the diaphragm cell method; it was first applied as a paper protector for the cathode and then became the covering of the entire cathode by applying it as a liquid and then creating a vacuum to seal it. The vacuum deposition of asbestos is one of the most important improvements of the chlor-alkali process (O'Brien and Bommaraju, 2005). By 1960 almost 60% of the U.S.'s production of chlorine was being carried out with these diaphragm cells, known as Hooker cells. Hooker cells incorporated asbestos deposition, as well as vertical cathode finger placement, both of which were main successes in increasing the efficiency of the industry. Over time the use of asbestos as a diaphragm cell became more prolific, and today an asbestos polymer mix is used (O'Brien and Bommaraju, 2005).

Mercury cell process

The mercury cell process is an alternative method to acquire chlorine and caustic soda that was developed in 1892, around the same time as the diaphragm cell process. It consists of two main parts: the electrolyzer and the decomposer (O'Brien and Bommaraju, 2005). The principal electrochemical reactions take place as follows:

In the electrolyzer:

Oxidation at the anode:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \tag{7}$$

Reduction at the cathode:

$$2Na^+(aq) + 2Hg(l) + 2e^- \rightarrow 2Na-Hg(l) \tag{8}$$

The net ionic equation:

$$2Na^+(aq) + 2Cl^-(aq) + 2Hg(l) \rightarrow 2NaHg(l) + Cl_2(g) \tag{9}$$

The "molecular" equation:

$$2NaCl(aq) + 2Hg(l) \rightarrow 2Na-Hg(l) + Cl_2(g) \tag{10}$$

In the decomposer:

Oxidation at the anode:

$$2Na-Hg(l) \rightarrow 2Na^+(aq) + 2Hg(l) + 2e^- \tag{11}$$

Reduction at the cathode:

$$2H_2O(l) + 2e^- \rightarrow 2OH(aq)- + H_2(g) \tag{12}$$

The net ionic equation:

$$2NaHg(l) + 2H_20(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Hg(l) \tag{13}$$

The "molecular" equation:

$$2Na-Hg(l) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + 2Hg(l) \tag{14}$$

The mercury cell process involves the flow of purified, saturated brine through a long, partially inclined tube. This tube is fit between a cocurrent stream of mercury and a grouping of electrodes, all covered by a gas-tight cover. During the electrolysis process chlorine is liberated at the anodes, as seen in the equations above, while the sodium ions are released at the surface of the mercury cathode to form a low concentration sodium amalgam, about 0.10–0.30% sodium by weight (O'Brien and Bommaraju, 2005). The purpose of this is so that the sodium is almost entirely prevented from reacting with the aqueous electrolyte to form caustic soda or with the dissolved chlorine to reform sodium chloride. This sodium amalgam then reacts with the water in the decomposer to form pure concentrated caustic soda (O'Brien and Bommaraju, 2005).

The mercury cell process was primarily developed by Hamilton Y. Castner, an American, and Karl Kellner, an Austrian. Castner's first mercury cell was flawed as it did not have a solution for the growth of caustic soda deposits. This was easily fixed by creating a cell that rocked back and forth. The two men's methods were applied in plants in the U.S. and England. A mercury cell plant in Niagara Falls, New York, was so successful because of its larger manufacturing capacity that its Castner cells were in continuous production from 1897 to 1960. After 1945 mercury cell capacities increased dramatically from 10 kA to 200–300 kA (O'Brien and Bommaraju, 2005). This large increase was due primarily to the integration of efficient silicon rectifiers, which replaced the mercury arc rectifiers. Other technological improvements were in the manner in which mercury was fed to the electrolyzer, the design of the decomposer, the support structure of the anodes and cathodes, the types of cell covers, and mercury inventory requirements (O'Brien and Bommaraju, 2005). Although "Europe's chemical makers scramble to end mercury-based chlor-alkali production" (McCoy, 2015, p. 25), it is still, currently, a large part of the industry.

Membrane cell process

The last major method for production of chlorine is membrane cell technology. This is an alternative to diaphragm and mercury cell production; it is a reworking of the diaphragm cell method so that the diaphragm is a permselective ion-exchange membrane. This membrane inhibits the passage of chlorine ions (negatively charged), but allows sodium ions (positively charged) to move through freely (O'Brien and Bommaraju, 2005). In this process sodium or potassium brine is fed to the cell and distributed equally throughout the anode compartments while water flows into the cathode compartments. The electrolysis reactions in this process are the same as they are in the diaphragm cell process. As the brine is depleted it overflows with chlorine gas into an anolyte header and the caustic soda that is produced overflows with hydrogen gas into a catholyte header.

Research on this method began in the 1940s and headway was made in the mid-1950s and 1960s conceptually, but practical problems with the system halted progress. No advancement was made for about 10 years, until in the late 1960s environmental problems associated with the mercury cell process revitalized interest in the membrane technology. Slowly factors that had been major problems in the early stages of development of the method were addressed and overcome, including erosion of anodes and membrane cell efficiency. The early 1970s brought the first two membrane cell technology commercial plants in the U.S., in Ohio and Alabama, and by the late 1970s membrane cell plants were producing mass amounts of chlorine (O'Brien and Bommaraju, 2005). During this time Japan became the main producer of chlorine using membrane cell technology in order to adequately address concerns of pollution caused by the mercury and diaphragm cell methods. The first membranes that were manufactured worked only at low caustic concentrations, but today's membranes are made of a perfluorosulfonate polymer layer, a polytetrafluoroethylene (PTFE) reinforcing fabric, and a perfluorocarboxylate polymer, bonded together (O'Brien and Bommaraju, 2005). This combination allows for low electrical resistivity and for low caustic back migration, which ultimately creates a more efficient and productive system (O'Brien and Bommaraju, 2005).

Effects of the industry

These three processes are the only methods used commercially for producing chlorine and caustic soda. As mentioned earlier, the top three producers in the chlor-alkali industry are Western Europe, the U.S., and Japan. In Western Europe 55% of the chlorine produced is done through the mercury cell process (European Commission, 2000), in the U.S. 75% of its production is done through the diaphragm cell process (European Commission, 2000), and in Japan, more than 90% is produced by the membrane cell process. The major necessary input required for the chlor-alkali industry is energy. Electrical energy is the integral part to the entire process. The main pollutant outputs that are produced from all three methods are chlorine gas emissions, free oxidants into water, such as Cl_2, Br_2, and hypochlorite, cooling agents, and general impurities that are removed during the electrolytic process (European Commission, 2000). The issue raised by chlor-alkali process is that two of these processes produce and use harmful chemicals, which result in dangerous work environments and harmful pollution. The diaphragm cell process relies on the use of asbestos and the mercury cell process on mercury. These two chemicals account for the highest environmental dangers from the industry.

Also worth mentioning is the toxicity of sodium hydroxide. Sodium hydroxide, also known as caustic soda, is the other product of these electrolytic processes (European Commission, 2000). At one side of the cell, the anode, the end product is chlorine (Cl_2), and at the other side, the cathode, it is caustic soda (NaOH). They are produced at the molar ratio of 1 mol Cl_2 : 2 mol NaOH. Since Cl and NaOH have molar masses that are close, 35.45 and 40.00 g/mol respectively, for every ton of Cl_2 produced 1.128 tonnes of NaOH are produced (European Commission, 2000). Caustic soda is a white noncombustible powder that absorbs water from air and is extremely corrosive; this makes its production a dangerous process (Agency for Toxic Substances and Disease Registry, 2014). It can cause severe burns when applied to the skin or eyes, or when ingested, and it is extremely damaging to aquatic ecosystems (Axiall Corporation, 2013).

Asbestos is composed of mineral fibers found in rocks that, in the chlor-alkali industry, are used in the concrete diaphragm cell for its strength and functionality at high temperatures. Exposure to asbestos fibers, such as chrysolite, has resulted in a high incidence of lung cancer, and, like arsenic, asbestos can act independently or combine with tobacco smoke to cause lung cancer (Hubaux et al., 2012). The development of lung cancer is three times higher among those who have been exposed to asbestos fibers (Hubaux et al., 2012). The diaphragm cell process, where asbestos is used, is the primary form of chlor-alkali process used in the U.S., one of the few countries that have not banned the use of asbestos in the chemical industry. In fact, the US EPA allows asbestos in the concrete that is used for the diaphragm cell process (US EPA, 2015). The main occasions of asbestos emissions in the diaphragm cell process are during diaphragm deposition, treatment of operating cells with asbestos slurry, and asbestos disposal (US EPA, 1995). Since the acknowledgment of asbestos as a carcinogen and pollutant, the U.S. chemical industry has taken steps to address its extreme use. These steps include trying to implement non-asbestos diaphragm cells or to adopt the membrane cell process.

Mercury is the main pollutant that is of concern in the chlor-alkali industry. Liquid mercury is used in the mercury cell process to form a mercury amalgam with sodium. It is harmful to individuals who ingest or inhale it. Vapor of elemental mercury is absorbed through the lungs and is then oxidized in the blood stream as Hg^{2+} (Barregård et al., 1990). Mercury vapor can be very harmful in its elemental form as it can pass the blood-brain and placental barriers. The central nervous system is at risk as well. The European Union has made drastic decreases in its mercury emissions in the past 20 years and also decreased the number of mercury cell plants from 91 to 44 (Euro Chlor, 2015). The World Chlorine Council reported that global mercury emissions are down from 24.6 tonnes per year to about 5.6 tonnes per year, approximately a 77% decrease (Euro Chlor, 2015). However, the fact is that some level of mercury pollution is guaranteed, but if properly regulated it can be controlled to the point where exposure is minimal.

There have been multiple cases of mercury pollution from industry. The most widely known is the case of Minamata, Japan, where mass poisonings and deaths were caused by mercury pollution between 1950 and 1975 (Mousavi et al., 2011). Monomethylmercury is a neurotoxin that causes Minamata disease (Mousavi et al., 2011). The poisoning resulted from the consumption of locally caught fish that had been contaminated by wastewater from factories disposing of mercury (Mousavi et al., 2011). Another case of mercury pollution occurred in Lake Managua, Nicaragua, from a chlor-alkali plant owned by a foreign corporation that used the mercury cell process. Due to its unsafe and reckless operations the plant knowingly disposed of 40 tons of mercury into Lake Managua, where the plant was located (Hassan et al., 1981). The plant was unregulated, and its workers were uneducated about how to work with dangerous chemicals and the possible effects of working with mercury (Hassan et al., 1981). It is reported that of the 152 workers, 37% suffered from mercury poisoning (Hassan et al., 1981). Due to poor working conditions and lack of maintenance, workers were exposed to mercury emissions into the air. The levels of airborne mercury were 600 $\mu g/m^3$ (Hassan et al., 1981). This is six times higher than the U.S. Occupational Safety and Health Administrations airborne standard, set at 100 $\mu g/m^3$ (Hassan et al., 1981). It is reported that 12,000 tons of mercury are currently contained in mercury cells used for the production of chlorine across Europe (European Commission, 2000). When the plants are eventually converted or shut down, there is no European Union policy on how to deal with that large a scale of a dangerous chemical (European Commission, 2000).

Another part of the discussion is that the diaphragm and mercury cell processes are both technologies that have stayed relatively the same for the past 40 or more years. This has allowed them to become outdated not only in their pollution emissions, but also in the amount of electrical energy they use. All three methods are electrolytic; thus, their largest input factor is energy. The distinctive part of the membrane cell process is that it is the most energy efficient and also uses neither asbestos nor mercury (European Commission, 2000). When compared with the diaphragm cell process, the membrane cell process uses about 1000 kWh/t less NaOH, and about 600 kWh/t less NaOH than the mercury cell process (Koter and Warszawski, 2000). The membranes used in this process efficiently use electrical currents and also yield a quality product with a typical contamination of NaOH with less than 50 ppm of NaCl (Koter and Warszawski, 2000). Japan is the only country of the three major producers that has made an effort to fully integrate this method into its chemical industry. Japanese producers have eliminated their use of the mercury cell process and use the membrane cell process for over 90% of their chlorine and caustic soda production (European Commission, 2000). Since 1975, membrane technology has increased dramatically and has become the most economically advantageous option in recent years. The switch to that method, however, has been slow, as many chlorine plants were built in the 1970s and have a life of approximately 40–60 years, and there has been no motivation through legislation to encourage any change until very recently (European Commission, 2000).

It was only in 2015 that the European Union announced a ban on mercury in its chlor-alkali industry (McCoy, 2015). The end of mercury-based production in Europe is December 11, 2017 (McCoy, 2015). This has many chemical companies rushing to build new facilities to accommodate this new requirement. It is a beneficial change, but a difficult and expensive one. Many companies are finding, during this process, that not only do they have to convert to membrane or asbestos-free diaphragm cell processes, but that there are large amounts of soil and groundwater mercury pollution around their plants (McCoy, 2015). Projects of expansion are turning into projects of remediation and cleanup. Also, the hundreds of tons of mercury in cells across Europe will have to be addressed and disposed of responsibly. This will have effects on the chemical industry as a whole, since it will be more affordable to close many plants than to convert them to the new technology. This ruling is a groundbreaking change, as Western Europe is the major producer of chlorine through the mercury cell method.

Although the membrane process is a much more efficient and environmentally friendly method, it has one characteristic that makes it of concern: its need for much higher quality brine (Basu et al., 2013). Brine for the mercury and the diaphragm cell processes contains less than 4 ppm of calcium and 0.5 ppm of magnesium (Office of Energy Efficiency and Renewable Energy [OEERE], n.d.). The membrane cell method requires a much purer brine solution, less than 20 ppb of calcium and magnesium combined (OEERE, n.d.). What this means is that there is a higher amount of effluents and brine sludge that is formed. Brine sludge contains NaCl, KCl, $CaSO_4$, $BaSO_4$, and water (Basu et al., 2013). Brine sludge from the mercury and diaphragm processes is hazardous, but brine sludge from the membrane cell process is not (Basu et al., 2013). The concern about the membrane cell's brine effluents, as well as those of the other two processes, lies in their ability to salinize soil and water, which can cause both to be infertile (Duffus and Worth, n.d.).

Conclusion

Since the 1940s chlorine production has skyrocketed with the sharp increase in demand for plastic. With this, the need for efficiency and emission awareness is of great concern. Electromembrane processes, like the membrane cell process in the chlor-alkali industry, are proving themselves to be efficient and environmentally friendly alternatives (Koter and Warszawski, 2000). It is projected that after the European Union's transition out of the mercury cell process, membrane cell methods will account for almost 80% of the world's chlorine production (McCoy, 2015). This is up from 18% in 1990 (McCoy, 2015). The chlor-alkali industry is an extremely important part of the commercial chemical complex, and the use of asbestos and mercury within it needs to be addressed on a large scale. As we can see from Europe's decision, technology for efficient and environmentally conscious production is available, and it is up to the major producers and legislators to take steps to phase out harmful methods and implement responsible and chemically sustainable alternatives.

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Alternative Energy Sources and Technologies for the Pulp and Paper Industry

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ABSTRACT

Weyerhaeuser—together with Amoco Corporation, Carolina Power and Light, and Stone and Webster Engineering Corporation—carried out a feasibility study sponsored by the National Renewable Energy Laboratory and the Electric Power Research Institute to assess the economic merits of expanding the use of biomass at its New Bern, North Carolina, facility to produce electric power and liquid fuels. Biomass gasification is expected to be a means for improving utilization of wood and process wastes while producing gas turbine fuel and reducing environmental impact. The team also assessed the technical merits and business potential of integrating a nominal 1000 ton/day biomass processing facility to produce ethanol at the New Bern plant. The primary objectives were to evaluate biomass as a source of electric power and liquid fuels within the context of a specific operating pulp mill and to assess the relative value of biomass-derived electric power and liquid fuel. An additional objective was to define the most cost-effective process for commercializing advanced biomass to energy technologies. This article describes the conditions that make these technologies potentially attractive, outlines the approach taken to develop comparative economics and economic sensitivities, presents results of the analysis, and suggests options for proceeding to commercialization of these advanced conversion technologies.

Index Entries: Biomass; pulp industry; paper industry.

INTRODUCTION

Driven by process changes that are making pulp and paper mills ever increasingly dependent on purchased electric power, the industry is motivated to search for technology alternatives for the conversion of its biomass residuals to electricity and other useful energy products. Recent emphasis by the US Department of Energy in the area of renewables has provided an unusual window of opportunity for advancing to commercial viability this new more efficient energy-generation technology. This window of opportunity comes at a time when greater than 50% of the industry's power generation equipment will need major alteration or replacement in the next 15 yr, as a result of age.

Two technologies that can have a profound impact on the industry's or energy self sufficiency—even to substantially increasing the capability for Axle exporting electric power—have evolved to the point of commercial readiness. These technologies are biomass gasification combined cycle (BGCC) and black liquor gasification combined cycle (BLGCC). A third technology, ethanol production from biomass, although not as advanced in its commercial readiness, is also of increasing interest driven by recent advances in fermentation technology and a significantly increased market opportunity as a result of the environmental need for gasoline additives.

Black liquor gasification is being actively pursued by Weyerhaeuser and others and is not considered here. This paper compares, for an integrated pulp mill situation, the operating and economic realities of BGCC and biomass-to-ethanol technologies. As partners in the project, Amoco supplied the ethanol production technology input and marketing analysis; Stone and Webster Engineering of Boston provided the cost estimating and economic analysis; and Carolina Power and Light provided the power market information pertinent to North Carolina. The study was made possible through the NREL-EPRI sponsored "LOI" program.

Economic information presented here includes sensitivities to export power price, feedstock price, DOE capital support and, in the case of ethanol, additional sensitivities to ethanol price and enzyme cost are presented. The project report presented to NREL and EPRI contains additional information. Analysis of these sensitivities indicates that, in the case of ethanol, the market price and enzyme cost are by far the most influential in determining the project viability. Enzyme costs less than $4/gallon and/or ethanol prices of approx $1.40/gallon appear necessary to move the ethanol concept as presented here into an economically interesting range. It should be noted, however, that the state of development of biomass to ethanol is clearly precommercial at this time and that a number of design improvements that would significantly change this picture are possible. Also, if a high value marketable product can be developed for the lignin stream, this would have a very significant positive impact.

Based on the analysis of sensitivities with respect to gasification, capital cost and, in this case, the value of export power, have by far the most, significant impact on BGCC economics. Given a 50% shared cost for the first commercial plant, a positive economic result is achievable at export power prices of 5¢/kWh and above. It is Weyerhaeuser's belief that these BGCC results—coupled with the future possibilities of integrating this technology with BLGCC, the probability of a mature BGCC technology having 20–30% less capital cost, and anticipated trends in electricity prices—make biomass gasification combined cycle a viable, even exciting, future possibility that should receive early support for commercialization. With shared cost through DOE's commercialization programs similar to the current request for proposals advanced in the Biomass Power for Rural Development solicitation, BGCC should find an early home in the forest products industry, contributing to the country's energy self sufficiency from renewable resources and improving the industry's global competitiveness.

A LOOK AT THE FOREST PRODUCTS INDUSTRY OPERATING ENVIRONMENT

This is a time of great dynamics for the Forest Products Industry. There are a number of converging events occurring in and around this industry that will encourage, if not mandate, changes in the way the industry designs, builds, finances, and operates its process plants. The discussion here focuses on how these changes will impact the way the biomass utilized by the industry is acquired and converted to useful energy products as we enter the next century.

To set the stage, six of the converging events that are clearly impacting the industry are:

1. Increased dependence on purchased electric power: Improved efficiency of steam use and related reduction in byproduct power generation, increasing needs for environmental equipment, trends toward more thermomechanical pulps and recycling, new bleaching technologies, and other process changes all impact the pulp and paper mill steampower balance with a clear trend toward more purchased power per ton of product produced even though, in most cases, total energy use per ton has decreased.
2. Aging of kraft and hog boilers: The industry's expansion and capital replacement cycle has produced a set of power houses, the majority of which are 20–30 yr in age, that will need replacement or at least major alteration in the next 5–15 yr.
3. Tightening air emission regulations: The new emission rules currently being discussed with the EPA will greatly impact how the industry has historically operated its facilities as well as significantly increase its capital commitment.
4. Necessity for improved capital performance: As the most capital intensive industry in the industrial sector, future process changes and process equipment needs must cost less and deliver more if the industry's attractiveness to investors and global competitiveness is to be maintained.
5. Increased emphasis on renewable energy: In spite of great political pressure to significantly change government, including the US DOE, the country's again-growing dependence on imported fuels and increasing environmental pressures will, most believe, maintain the emphasis on renewable energy at all time high levels. The forest products industry has a unique opportunity to continue to lead the nation in the utilization of renewables.
6. Availability of emerging technologies: The best—and perhaps the only—time when new technologies can easily be adopted by a capitally intensive industry is when that technology is commercially available at a time when the normal capital replacement cycle mandates major system repairs or replacement. With respect to power and recovery systems, this situation may very well be about to exist.

It is not at all inconceivable that the power house of the next decade will see the conventional recovery and power boilers rapidly being replaced with BLGCC and BGCC or IGCC technologies and, in many cases, exporting significant quantities of electricity or liquid fuels. In making this change, the industry can nearly double the efficiency by which it produces useful energy as shown in Fig. 1 and become significantly more self sufficient on renewable sources. (A simple schematic of how this future power house might look is shown in Fig. 2.)

DESCRIPTION OF THE NEW BERN MILL

One of the primary objectives of this study was to look at the gasification and ethanol technologies in the context of a real operating pulp mill. Issues associated with integration with existing plants have been postulated in prior studies but, to the knowledge of this project team, an actual integrated mill study had never been

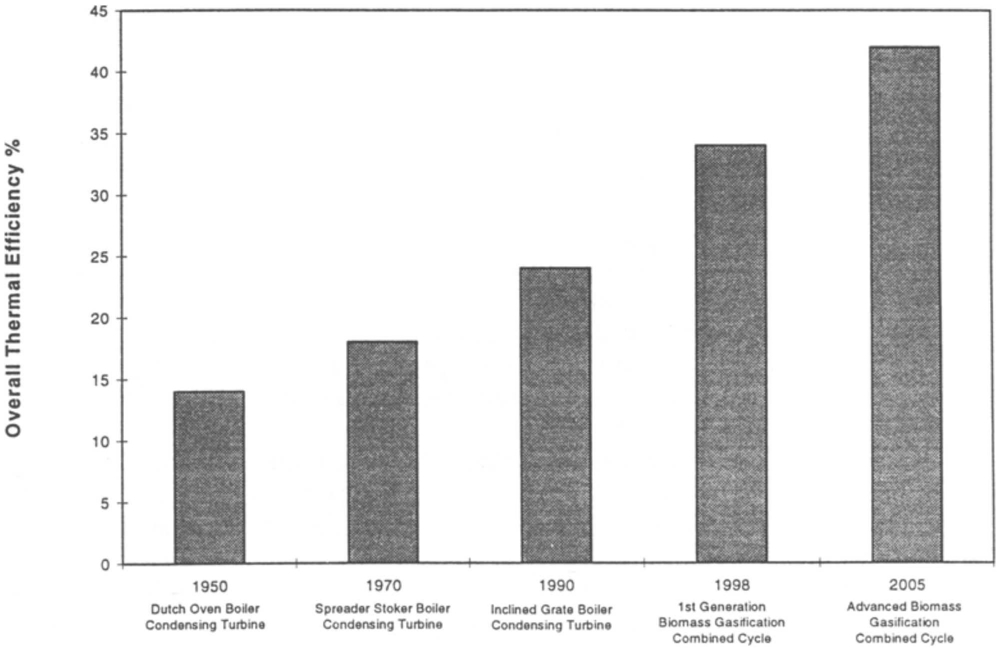


Fig. 1. Power generation efficiency comparison.

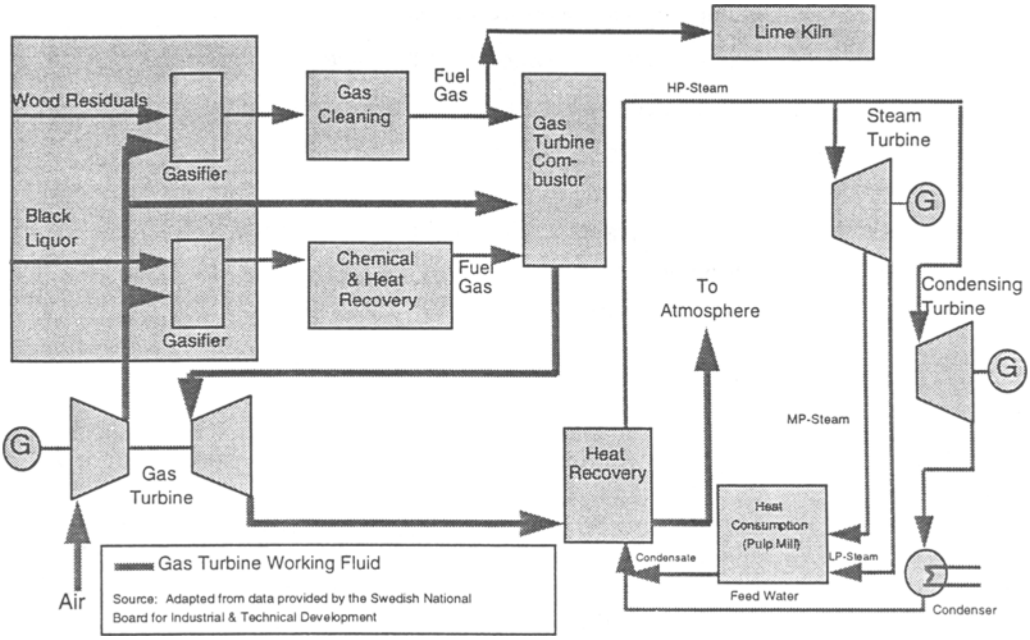
completed. The Weyerhaeuser bleached market pulp mill at New Bern, NC, was selected for the feasibility study. The mill has had a continuing interest in gasification technologies for many years. The New Bern Pulp generates process steam and electricity using a black liquor recovery boiler, a power boiler, and an extraction backpressure steam turbine generator. The power boiler, although designed to burn mill residuals (rejected or waste biomass), is currently able to fire only oil as a result of emissions limitations. The mill has evaluated the possibility of life extending (modifying) the power boiler and retrofitting emission controls, which would allow it to once again burn biomass. This boiler modification project is used as the base case for economic comparisons made with BGCC and ethanol technologies. A BGCC cogeneration plant or a combined BGCC-EtOH plant could be an alternative to the bark boiler modification project.

A General Electric Frame 6B gas turbine was selected as the basis for the BGCC plant evaluated in this study, since a biomass gasifier firing the 6B gas turbine with a heat recovery steam generator (HRSG) is of the right size to meet the steam requirements of the mill for the foreseeable future.

The pulp mill and associated saw mill produce approx 129,000 BDT/yr of biomass wastes. A BGCC project would require additional biomass feed to be supplied from forest management thinnings and other sources that are discussed in more detail below.

THE COST AND AVAILABILITY OF BIOMASS FUELS (FEEDSTOCK)

Feedstock or fuel cost and availability were also a major part of the feasibility study. The feedstock assessment was undertaken with the full involvement of



Source: Adapted from data provided by the Swedish National Board for Industrial & Technical Development

Fig. 2. Power-recovery island of 2010.

Weyerhaeuser's forestry research and raw materials people and drew from TVA and US Forest Service databases as well as company internal sources. Six possible strategies were considered, including a range of possibilities from utilizing existing residuals through managing plantation systems to produce significant additional quantities of material for energy while enhancing the sites productivity for wood and pulp products. These six strategies are shown in Fig. 3.

The first of these strategies involving company-controlled wood residuals is the simplest and most obvious to take advantage of since the material is already owned by Weyerhaeuser and, in the case of New Bern, is already on the mill site. The handling costs are the only incremental costs and the existing value is what other people are willing to pay for the fuel, less transportation costs. Approximately 110 kBDT/yr fall into this category with an additional 100 kBDT/yr within reasonable hauling distance of New Bern.

The second strategy involves utilizing the gasification or ethanol facility as a disposal opportunity for on-site generated sludges and other combustible material. This is a very small amount of material on a bone dry basis, but could reduce disposal costs for the mill. The implementation of this strategy would require a suitable drying technology and is not of significant energy value.

The third strategy, which involves the capture of residual chips from final harvest and plantation thinnings from current plantation operations both owned by and available to Weyerhaeuser, represents a very significant fuel opportunity. Though not necessarily the lowest cost, the woods residual component from natural stand final harvest is the single largest source of biomass for fuel identified in this study. It conservatively amounts to at least 600 kBDT/yr and, based on Weyerhaeuser's experience, could run significantly higher within a reasonable hauling distance of New Bern.

1) Company-controlled wood residuals
2) Mill produced non-woody combustibles
3) Energy fiber from present plantation operations
4) Maximize production of current plantation monoculture
5) Intermingle fast-growing species with plantation monoculture
6) Dedicated crops

Fig. 3. Six possible feedstock strategies.

Strategy 4 involves the growing of maximum pine volumes per acre while attempting to improve plantation productivity for primary pulp and wood products. Based on current operating approaches and currently available technology, the site-preparation cost for this approach is much too high (in excess of $50/BDT) and would require changes in approach and/or technology to become viable. The conclusions of this analysis should be of particular interest to those considering the establishment of softwood dedicated crops similar to the Southern Pine species found in North Carolina.

Strategy 5 involves growing maximum hardwood per acre intermingled with pine in existing plantations. Both hardwood sprouting between rows and hardwood inter-row plantings were considered. Again, with current technology there would be high plantation establishment costs and high harvesting costs to generate reasonably low volumes, such that this strategy also does not appear feasible with current approaches.

The sixth and final strategy involves the growing of maximum biomass per acre with a dedicated short rotation crop using mill and other locally available waste water as nutrient. Given the present understanding of fast-growing species tailored to eastern North Carolina, Weyerhaeuser foresters believe that even in this approach the Loblolly Pine would be the currently preferred species. Based on projections of growth and volume coupled with the expected planting, site preparation, and harvesting costs, this approach would become attractive at fuel values of ~$50/BDT. A number of factors—such as subsidies for waste water disposal, development of a genetically improved, faster growing crop, improved harvesting approaches, and so forth—all could reduce this fuel value. The development of these possibilities is beyond the scope of this study, particularly given the fact as discussed in the next paragraph that sufficient material is available without these measures.

The study determined the availability of feedstock material as a function of cost for each of these strategy. Costs for supplying fuel ranged from $20/BDT to over $50/BDT delivered to the energy facility at New Bern. Feedstock material availability was significantly greater than required to meet the needs of the study's three energy design alternatives (up to 350,000 BDT/yr) and can be provided at an average cost of less than $25/BDT. When only material sources which cost less than $35/BDT and could be quantified and confidently identified as available or unused were included, the amount exceeded 940,000 BDT/yr. This excess material avail-

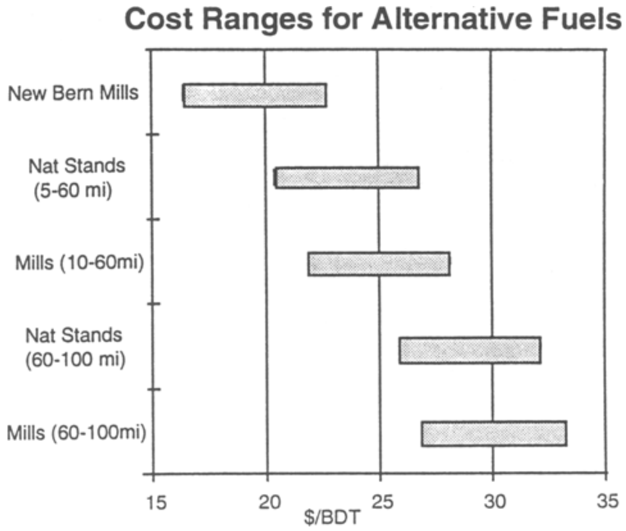


Fig. 4. Company-controlled wood residuals. Capture existing volumes of wood residuals: company-controlled wood residuals, 272,000 BDT; external forest residuals, 598,000 BDT; external mill residuals, 13,000 BDT.

ability provides a significant margin of safety if byproduct residuals are reduced through efficiency improvements in harvesting or primary product recovery.

In addition, there is a significant quantity of mill residual material (up to 160,000 BDT/yr) within 40 miles of New Bern that is currently utilized by others and could be available because of its close proximity to New Bern. This material would cost less than $25/ BDT, but was not included because of the associated uncertainty in cost and quantity. The primary sources proposed for use include residuals from Weyerhaeuser mill facilities at New Bern and within 60 miles of New Bern and forest residuals from final harvest operations.

The bottom line is that there is fuel available in the New Bern area at under $25/BDT for the foreseeable future in the amounts needed for the size plant under consideration. Although current approaches to plantation establishment and harvest recovery are too expensive to provide only biomass fuel from "energy plantations" or from planting additional trees for fuel, improvements in technology could make future combination fuel and fiber plantations viable. The approach and detailed results of this feedstock analysis are included in the final report to NREL and are summarized in Figs. 4 through 7.

FEASIBILITY OF BGCC

Working as part of the NREL-EPRI sponsored "LOI" program, Weyerhaeuser, Amoco, Carolina Power and Light, and Stone and Webster Engineering have, over the past year, completed a detailed feasibility study of the economic and operational realities of both BGCC and biomass-to-ethanol technologies. The study was focused on the New Bern, North Carolina, mill and associated dedicated feedstock system (DFSS). This mill already has a history of investigating black liquor gasification technology. The gasification technologies are discussed below.

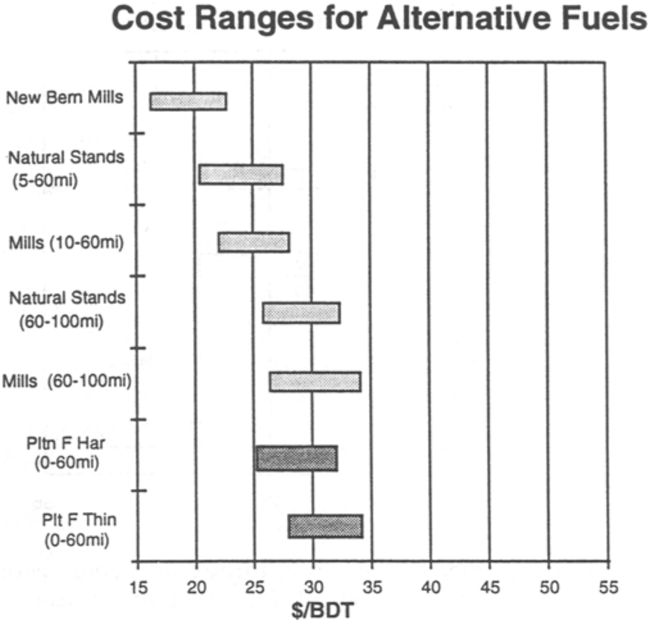


Fig. 5. Energy fiber from present plantations. Energy fiber from present plantations: 58,000 BDT.

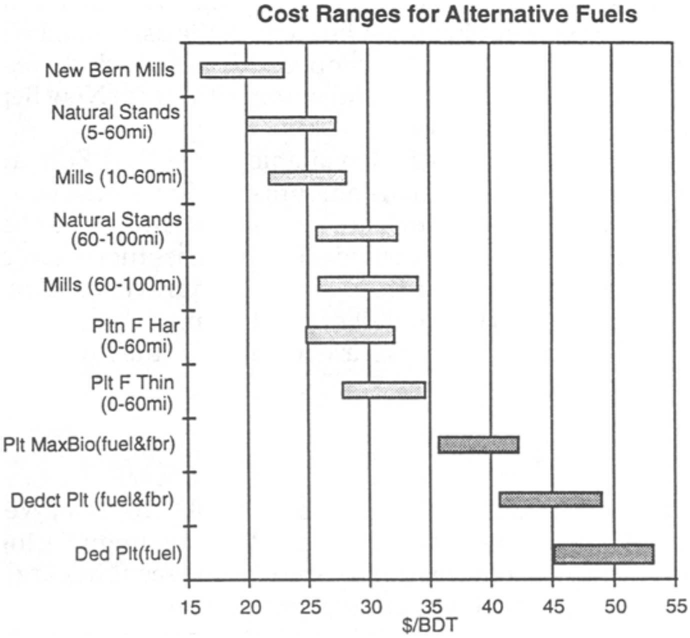


Fig. 6. Alternative fuel options. Maximize current plantation production; intermingle fast-growing species; dedicated crops.

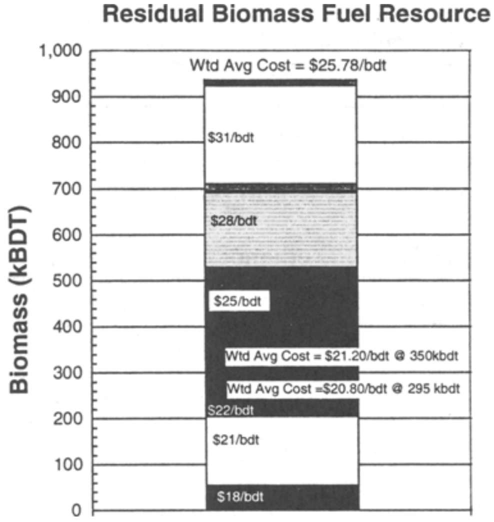


Fig. 7. Primary fuel sources for New Bern.

Leading suppliers offering biomass gasification systems include:

- Ahlstrom: pressurized (~20 bar) recirculating fluid bed;
- Tampella: pressurized (~30 bar) spouting bed;
- TPS: atmospheric sequential two-stage fluid bed; and
- FERCO/Zurn-Nepco/Battelle: atmospheric indirect two-stage fluid bed.

Also studied but not investigated in detail were American Carbons/Kaiser, Lurgi, and Noell.

Each of the suppliers mentioned above has commercial or near commercial offerings. Angstrom is operating a 15 MW$_{th}$ BGCC plant at Värnamo, Sweden, and is participating in a design competition for a project in Brazil. Tampella operates a 15 MW$_{th}$ gasification plant on biomass and coal at Tampere, Finland, on an intermittent basis and is prepared to make commercial offerings of both biomass and coal as well as combined systems. TPS has operated a 2 MW$_{th}$ facility at Studsvik, Sweden, for a number of years and is also a participant in the Brazilian project. The pilot 2 MW$_{th}$ Battelle gasifier has logged the most operating hours of any system with well over 20,000. Currently FERCO and Zurn/Nepco are engineering a 40 MW$_{th}$, BGCC plant to be integrated into the biomass plant at Burlington, Vermont.

After discussing BGCC options with these seven potential suppliers, Tampella and TPS were selected for in-depth analysis. The ability to work with these two suppliers provided an excellent opportunity to contrast a pressurized system represented by the Tampella technology with an atmospheric system represented by the TPS technology. Given the degree of accuracy of this analysis, the capital cost and heat rates of the two technologies investigated were sufficiently similar that no clear preference of one over the other could be determined based on these factors alone. However, since the operating efficiency of the pressurized technology was higher, the Tampella case was taken forward for detailed economic analysis. It should be noted, however, that the pressurized system eliminates the possibility of a staged implementation, which is the preferred approach at the New Bern facility.

Table 1
Capital Costs of Cases Considered

Case	Cost
Base Case	$21,100,000
BGCC with 33.4 MW export power	$97,930,000
BGCC/ethanol with 19.5 MW export power plus 70,000 GPD ethanol	$189,802,000
Ethanol only with 79,000 GPD ethanol	$117,930,000

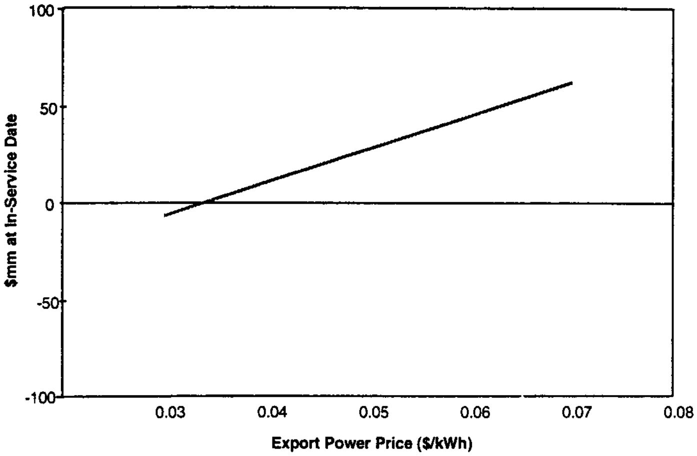


Fig. 8. Sensitivity of incremental plant's NPV to power price (50% capital support). NOTE: Assumes feedstock cost of $14/wet ton. Zero line represents NPV @ 12% and 20 yr compared to base case power boiler conversion with condensing turbine.

These gasification technologies were compared with the Amoco biomass-to-ethanol technology. Three designs were considered:

1. BGCC with 33.4 MW export power;
2. BGCC/ethanol with 19.5 MW export power and 79,000 GPD ethanol; and
3. Ethanol only with 79,000 GPD ethanol production.

In all cases, the energy needs of the New Bern mill were satisfied. The capital cost of the base case and the three cases described here are shown in Table 1.

The attractiveness of the BGCC technology is significantly impacted by the capital cost of the plant, the value of the power produced, and the cost of the feed stock These impacts are shown in Figs. 8 through 10. These sensitivities are portrayed as incremental net present values relative to operating the New Bern mill as it is configured today. By looking at the results in this way, the difficult and often controversial task of assigning costs and values to all streams crossing the powerhouse boundary is avoided. The zero NPV line on these curves is calculated at 12% return on capital invested over a period of 20 yr and is believed to be a somewhat normal investment yardstick for evaluating investments within the industry. In layman's terms, anything falling below the zero line would likely be considered a bad investment, a project falling on or near the positive side of the zero line would likely be considered a marginal investment and projects falling well above the zero line would likely be considered an interesting investment possibility.

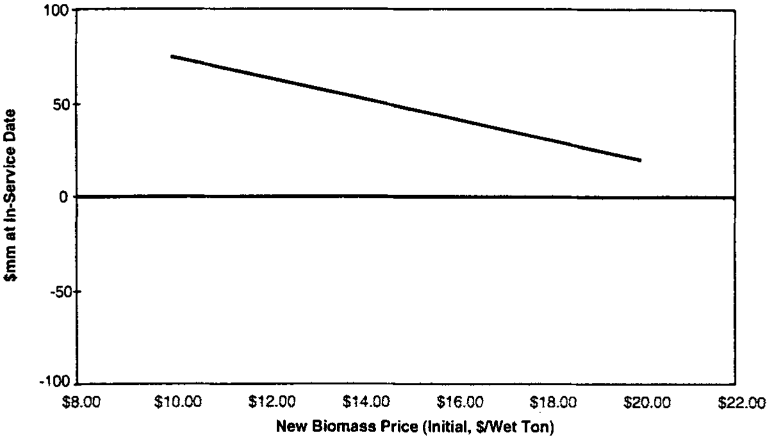


Fig. 9. Sensitivity of incremental plant's NPV to initial biomass price (50% capital support). Economic sensitivity—cost of feedstock. NOTE: Assumes power sale price of $0.05/kWh. Zero line represents NPV @ 12% and 20 yr compared to base case power boiler conversion with condensing turbine.

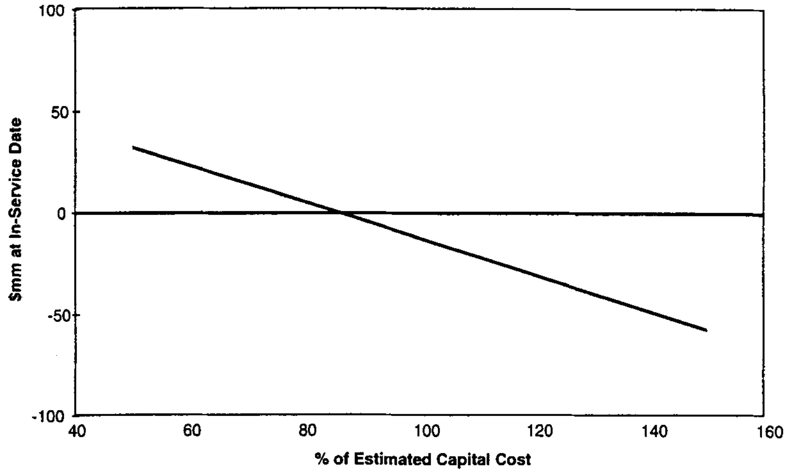


Fig. 10. Sensitivity of incremental plant's NPV to capital cost. NOTE: Assumes feed stock cost of $14/wet ton and power sales price of $0.05/kWh. Zero line represents NPV @ 12% and 20 yr compared to base case power boiler conversion with condensing turbine.

Since the current operating situation at New Bern is somewhat unique, a second comparison was made—this time utilizing a new greenfield multifuel boiler. This boiler is visualized as a bubbling or recirculating fluidized bed, capable of handling the same variety of feedstock that would potentially be utilized in the BGCC technology. The same comparison approach was utilized. Figure 11 shows the results of this comparison as a function of export power price.

A comparison with Fig. 8 shows an enormous similarity. However, in Fig. 8, a 50% capital support for the project was assumed; in Fig. 11, no such capital support is included. Therefore, an unsubsidized BGCC facility looks interesting at power cost above 3.5¢/kWh. It is important that a result of this nature appears achievable. If all future projects required a subsidy to proceed, it would be difficult to justify development dollars to commercialize the technology. However, given this analysis and the potential of the technology, BGCC appears well justified for commercial-

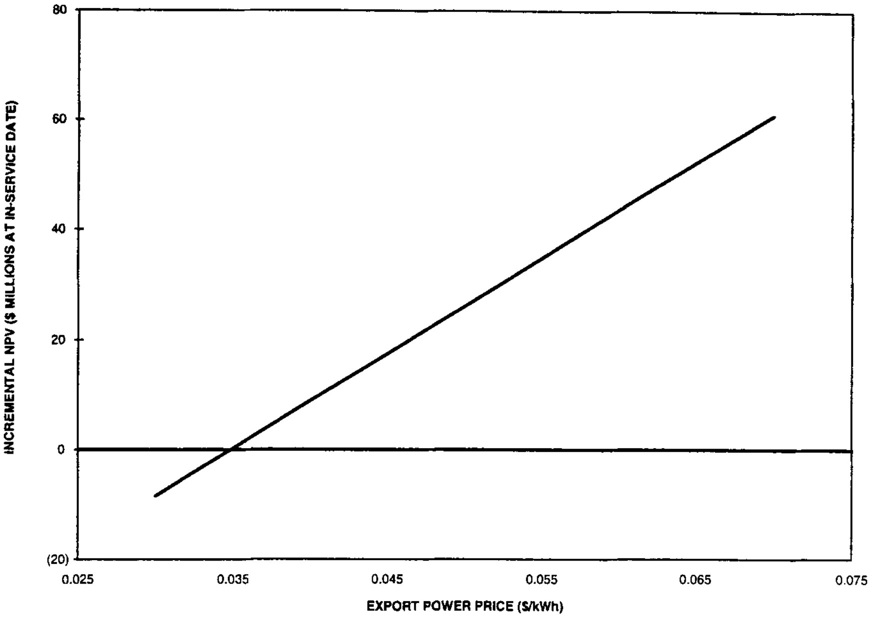


Fig. 11. BGCC compared to multifuel boiler base case—no capital support. NOTE: Assumes feedstock cost of $14/wet ton. Zero line represents NPV @ 12% and 20 yr compared to a multifuel boiler base case.

ization. Figure 12 taken from the EPRI "Technical Assessment Guide" presents an argument that capital cost reductions of 20–30% may be possible for this technology, based on the history of other developments.

Given that these reductions in capital cost are achievable as subsequent facilities are cost engineered and built—and that power values of 5¢/kWh and greater are realizable through power contracts, wheeling, or displacement of purchased power—the results of the study demonstrate that BGCC technology has significant potential for achieving improvement in pulp mill operation and biomass utilization efficiency. It also has the potential for developing additional product revenue streams, which could enhance for product industry economic productivity. These conclusions when coupled with the possibility of future integration of BGCC with BLGCC technology (*see* Fig. 2), the probability of these technologies at maturity being less capitally intensive than present plants and anticipated trends in electricity prices, make BGCC a viable and exciting future option.

FEASIBILITY OF BIOMASS TO ETHANOL

In addition to the commercial and economic realities of BGCC, Weyerhaeuser shared Amoco's interest in determining the site-specific feasibility of a biomass-to-ethanol facility. This part of the study was focused on determining how an integrated ethanol plant would compare with power generation, both as a stand-alone facility and in combination with a gasification plant that would utilize the reject lignin from the ethanol process. Assuming favorable economics, an additional objective was to enhance the understanding of the market for biomass-to-ethanol conversion technologies as related to the forest products industry.

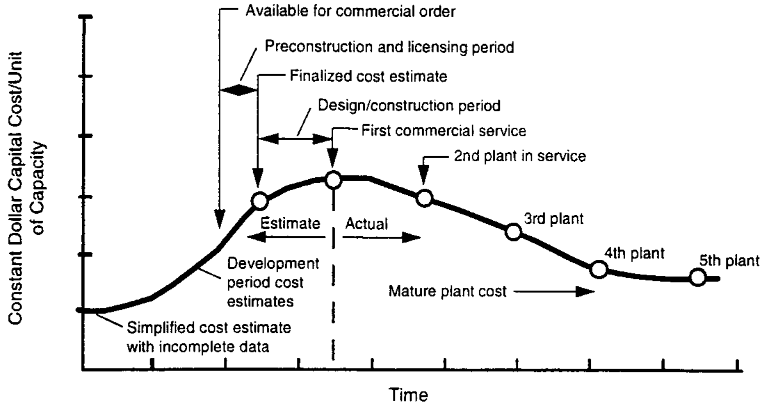


Fig. 12. Capital cost learning curve. Source: EPRI Technical Assessment Guide.

The basis for the ethanol plant design was being developed by Amoco, which is based on a proprietary pretreatment step followed by simultaneous sacrification and fermentation. The basic process utilized is discussed elsewhere in the literature. Sensitivity analyses were carried out in the same manner as discussed with BGCC. These studies indicated that project economics were most sensitive to enzyme cost and ethanol price. The sensitivity of the enzyme cost could very well influence the decision as to make or buy.

The details of this analysis are available in the report provided to NREL under the LOI contract. The basic conclusion to be reached is that, given the maturity of the technology and the anticipated benefits of on-site enzyme production, the economics for an integrated BGCC/ ethanol facility at a site similar to the New Bern mill become comparable with a BGCC plant alone at ethanol prices somewhere in the range of $1.25–1.40/gallon. This picture could be improved even further if a better use than energy could be found for the lignin byproduct.

CONCLUSIONS

Events that will impact the forest products industry over the next decade present a mandate for change in the way energy is provided and used in the industry's operating facilities. This is happening at a time when more environmentally benign and significantly more energy efficient technologies are becoming commercially available. In addition, options exist to significantly increase alternative feedstock availability and for producing valuable chemical byproducts. The industry has a unique opportunity to productively lead the nation in its goals for increased use of renewable energy and continue, if not enhance, its history of global competitiveness. One result will be that the power island of the future will utilize emerging BGCC and BLGCC technologies, cost less, and be substantially more efficient in energy conversion. As biomass-to-ethanol technologies are matured, there appears to be an operating range where the economics can be quite attractive. However, this range is highly influenced by site-specific factors such as the value of the lignin as an energy source, the capital cost of integration with the pulp mill, and by the cost of enzyme production and sale price of the ethanol. A final conclusion is that it appears and a combined ethanol and power integrated facility has a high probability of being more profitable than ethanol production or power generation taken alone.

Chapter

Alternative Raw Materials for Pulp and Paper Production in the Concept of a Lignocellulosic Biorefinery

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Abstract

The main source of cellulosic fibre used for pulp and paper production comes from wood, while non-wood fibres are used to a lesser extent. However, a renewed interest exists in the use of non-woody raw materials due to their abundance as source of low-cost fibres and because they are sometimes the only exploitable source of fibres in certain geographical areas, mainly in developing countries. Moreover, the great variety of characteristics, fibre dimensions and chemical composition of these alternative raw materials give them a great potential to produce different types of papers. On the other hand, the pulp and paper industry is an excellent starting point for the development of lignocellulosic biorefineries, possessing the necessary technology and infrastructure as well as extensive experience in lignocellulosic biomass transformation. Since its beginnings, the pulp and paper industry has been practicing certain aspects of the biorefinery concept, generating the energy necessary for the production of cellulosic pulp from the combustion of lignocellulosic waste and black liquors, recovering the chemical reagents used and generating high value-added products (e.g. tall oil) together with cellulosic pulp. However, the evolution of the pulp and paper industry to a lignocellulosic biorefinery requires technological innovations to make bioenergy and new bioproducts available alongside traditional products.

Keywords: alternative raw material, agricultural residues, annual plant (vegetables), pulp, paper, biorefinery

1. Introduction

Several successful industrial factories based on alternative raw materials for pulp and paper production already exist nowadays [1, 2]. Lignocellulose is the major structural component of plants and is by far the most abundant type of earthly biomass [1, 3]. It mainly consists of cellulose (40–60%), hemicellulose (10–40%) and lignin (15–30%), with minor amounts of extractives, proteins and inorganic compounds [1, 3]. Lignocellulose components can be found in both woody (e.g.

spruce, pine, eucalypt, poplar, etc.) and non-woody biomass, the latter including vegetables (e.g. bamboo, tagasaste, kenaf, abaca, etc.) and agriculture residues from harvesting and pruning operations (e.g. barley straw, wheat straw, orange tree pruning, olive tree pruning, etc.) and from agro-food industry [e.g. bagasse, empty fruit bunches from oil palm (EFB), etc.]. Cellulose is a linear and highly ordered polymer of cellobiose (D-glucopyranosyl β-1,4-D-glucopyranose), whereas hemicellulose represents a family of branched carbohydrate polymers containing both pentoses (e.g. xylose, arabinose) and hexoses (e.g. galactose, mannose, glucose) and showing often uronic acids (e.g. glucuronic acid) and acetyl moieties as sidechain groups [1, 3]. By contrast, lignin is a three-dimensional network buildup of dimethoxylated (syringyl, S), monomethoxylated (guaiacyl, G) and non-methoxylated (p-hydroxyphenyl, H) phenylpropanoid units, derived from the corresponding p-hydroxycinnamyl alcohols, which give rise to a variety of subunits including different ether and carbon–carbon bonds [4].

The main non-food use of lignocellulosic biomass is the production of cellulosic pulp from which a wide range of products can be obtained, highlighting the production of paper. At the beginning of the 1990s, there was the conviction that the arrival of new information technologies would reduce the consumption of paper; however the data of world consumption of paper and cardboard revoke this idea as it went from 240 million tonnes in 1990 to 413 million tonnes in 2016, of which 77.3 million tonnes are consumed in Europe [5]. In the past, the raw materials used in the manufacture of paper were herbaceous biomass such as flax, cotton, bamboo and cereal straw. It was not until the middle of the nineteenth century when woody materials began to be used, mainly due to the increased demand for paper because of the emergence and increased use of printing. Today, most of the cellulosic fibers used come from wood species, mainly hardwoods and softwoods [1, 2, 6]. Nevertheless, in recent years there has been an increase in consumer awareness of the need to preserve the environment, which is why they demand a more ecological production of paper, both in the use of raw materials and in manufacturing processes. With the same purpose, government bodies devote economic and human resources to research into alternative raw materials to conventional ones. For these reasons, a large number of studies on the use of non-woody materials, including agriculture residues and vegetables as alternative source for cellulosic pulp production, have emerged in recent years [1, 7–14].

Some of the advantages of using non-woody raw materials can be mentioned: (i) in developing countries with scarce forest resources, non-woody biomass provides an effective alternative to importing wood, paper, or cellulosic pulp. In these countries, there may be a large area devoted to food crops, which would provide considerable amounts of agricultural residues and agro-food industries [1, 15]; (ii) non-woody biomass increases the added value of agri-food crops by taking advantage of their residues (traditionally used for burning or agricultural amendments) to obtain a product in great demand such as paper [1, 15]; (iii) production of special papers, whose most suitable raw materials are certain vegetable alternatives to conventional woods [1, 16]; and (iv) since the morphological characteristics of the fibers and the chemical composition of the non-woody species are very varied, a wide range of papers can be obtained by properly selecting and/or mixing these raw materials [1, 14].

2. Availability of raw materials

The availability of raw materials is very important when approaching the industrial facility for the production of cellulosic pulp. Availability is related to the production and location of the various lignocellulosic materials that can be used for the intended purpose. In the case of agricultural residues from harvesting and pruning operations, it can be said that they are very abundant in Spain. Specifically, it is estimated that the production of the most important agricultural residues, due to their abundance, such as cereal straw, sunflower stalks, vine shoots, cotton stems, olive, orange and peach tree pruning and vegetable and other similar crop wastes, represents about 50 million tonnes per year, with Andalusia contributing with more than 20% [1, 17].

Due to its abundance, it seems that the most recommended agricultural residue for the manufacture of paper pulp is cereal straw since it represents almost 20% of the agricultural residues considered in 2007, and the technology used in its collection is fully developed [1, 17–19]. Regarding the waste from the agri-food industry used for the production of cellulosic pulp, the bagasse from the extraction of sugar cane and waste from the palm oil industry (EFB) should be highlighted [20].

With regard to alternative vegetables for cellulosic pulp production, they can be classified in three groups: (i) plants of wild nature such as bamboo, different types of cane, esparto grass, etc. [21]; (ii) plants from plantations with industrial uses, such as sorghum, abaca, sisal, jute, hemp, kenaf, flax, etc. [7, 22]; and (iii) other plants, mainly herbaceous species, grasses and legumes, which produce high biomass yields when grown in intensive plantations (tagasaste, *Leucaena* spp., etc.) [23–25].

3. Storage of lignocellulosic materials

The prolonged storage of lignocellulosic raw materials is always necessary in the pulp and paper industry. In the case of raw materials that are harvested only at a specific period of the year, the storage is even more important. Therefore, these raw materials must be collected in order to meet the annual needs of a factory, so that it operates all year round, with the consequent better use of installed capacity. On the other hand, many alternative lignocellulosic materials are more easily deteriorated due to their non-woody special properties, such as straws, herbaceous vegetables, etc., mainly if they contain high percentages of humidity. In fact, of all the factors that influence the storage of this type of sources, the most relevant is the residual humidity. Given that these materials do not require too rigorous conservation, as they are not intended for food, the rule of allowing slightly higher humidity than the “Caurie safety” humidity obtained by adjusting the experimental data on equilibrium humidity and relative humidity of the environment of the adsorption isotherms to the Caurie equation can generally be adapted. Applying this standard and observing the experimental adsorption isotherms, it appears that wheat straw, vine shoots and cotton stems can be well conserved in environments with relative humidity below 60–70%, while other agricultural residues such as olive tree pruning or sunflower stems require lower values [26]. On the other hand, it has been verified that the recommended maximum relative humidity values, according to the standard followed in this work, coincide with those obtained experimentally when storing the different agricultural residues considered in environments with different relative humidity for 10 or 12 months. As the chemical composition of these agricultural residues is considered as well as their fibrous structure does not differ so much from other agricultural residues such as wastes from agro-food industries, forestry residues and vegetable materials in general, the above conclusions can be extended to all these alternative lignocellulosic materials.

4. Characterization of lignocellulosic materials

Theoretically speaking any plant containing a reasonable amount of fibres can be used as a raw material for pulp and paper production. In practice, this is not the case. Besides the abundance of the plant, a steady supply and many other requirements are necessary. The fibre content of the plant is important. The plant contains in addition to fibres many non-fibrous cells, e.g. parenchyma cells. Fibres themselves vary much in different plants regarding their length, width, fine structures or microstructures, as well as their chemical composition. In one and the same plant, there are different types of fibres. The same fibre type is not equal in dimension but contains a spectrum of different dimensions. For this reason, one speaks of "average fibre length". The length of the fibre is one of the most important parameters affecting paper strength [1].

Chemical characterization, which gives rise to the percentages of the main chemical constituents of lignocellulosic materials (generally cellulose, hemicellulose, lignin, as well as extractives and ash), is of great interest since it can indicate their possible applications for obtaining cellulosic pulps, in terms of the most suitable process to follow and the type of pulp that can be obtained. In this characterization, the contents of holocellulose, lignin, α-cellulose, hemicellulose, and extractives in water, 1% soda and ethanol-benzene and ash are determined as the most important. For this chemical characterization, TAPPI test methods, including TAPPI T 204 om-88, TAPPI T 211 om-93, TAPPI T 222 om-88 [27], and NREL analytical methods (National Renewable Energy Laboratory NREL/TP-510-42168) are usually employed [28].

When comparing the results obtained by different authors, a good concordance is generally observed for each specific material. Sometimes discrepancies appear that can be attributed to the different procedures used as well as to the different origins and varieties of the raw materials considered. For example, the chemical characterization results obtained for rice straw were analysed and compared with (i) some agriculture residues from harvesting and pruning operations and from agro-food industry (e.g. olive tree pruning, wheat straw, sunflower stems, sorghum stems, bagasse, vine shoots, and cotton stems); (ii) some vegetables (e.g. *Leucaena colinsi*, *Leucaena leucocephala, Chamaecytisus proliferus*, *Retama monosperma*, *Phragmites* spp., *Arundo donax, Prosopis juliflora*, and *Paulownia fortunei*); and (iii) softwoods (pine) and hardwoods (eucalyptus) [23, 29]. From this comparison it could be deduced that:

- The value of the hot water soluble content of rice straw (7.3%) is lower than that of the rest of agricultural residues, except for bagasse and cotton stems; it is higher than the values found for the vegetables considered, except for *P. fortunei*, and higher than the values for pine and eucalyptus.

- The value of soda extractives at 1% of rice straw (57.7%) is higher than the values corresponding to the rest of agricultural residues and vegetable considered, as well as those of pine and eucalyptus.

- The content of ethanol-benzene extractives in rice straw (0.56%) is lower than that of the materials considered: agricultural and agro-food residues, vegetables, pine and eucalyptus.

- The ash content of rice straw (9.2%) is higher than the values presented by the rest of agricultural residues and much higher than the values of pine and eucalyptus.

- The holocellulose content of rice straw (60.7%) is similar to the value found for olive tree pruning and lower than the values found for the rest of the agricultural residues considered, as well as those of the alternative vegetables considered and those of pine and eucalyptus.

- The content of α-cellulose of rice straw (41.2%) is lower than the values presented by the cotton stems, *L. colinsi*, *L. leucocephala*, *C. proliferus*, *R. monosperma*, pine and eucalyptus; higher than the values corresponding to olive tree pruning, wheat straw, *Phragmites*, *P. fortunei*, *Prosopis juliflora*; and similar to the values of the other species considered.

- The lignin content of rice straw (21.9%) is similar to the values corresponding to the cotton stems, *L. leucocephala* and *R. monosperma*; lower than the values found for *Phragmites* spp., *A. donax*, *P. fortunei* and pine; and higher than those of the other species considered.

In the same way, following the same example of rice straw, the experimental data on its physical characterization, which determines the size of its fibers, are compared with those of other lignocellulosic materials such as wheat straw, sunflower stalks, vine shoots, cotton tree stalks, olive tree pruning, sorghum stalks and pine and eucalyptus woods. After a biometric analysis with the rice straw studied, it is concluded that the length of its fibers (1.29 mm) is similar to that corresponding to the stems of sorghum, superior to those of the other agricultural residues considered and to that of eucalyptus but inferior to that of pine.

In summary, it can be stated that the alternative non-woody materials under consideration have acceptable chemical and physical characteristics for the production of pulp and paper [30].

5. Cellulosic pulp production

The manufacture of cellulosic pulp consists of the separation of cellulose fibers, which are cemented by the middle wall, composed mainly of lignin using physical or chemical methods [1, 2, 6]. In order to obtain cellulosic pulps from alternative non-woody materials, different chemical classical processes have been used (using chemical reagents such as soda, sodium sulphate and sodium sulfite) and organosolv (using organic solvents). In general, non-woody raw materials have a less density and more porous structure and, also in most of the cases, less lignin content, which means less energy and chemical requirements for fibre separation during pulp production. In addition, they have shorter growth cycles, reaching maturity faster than wood species, and in many cases the pulp yields obtained are higher [30].

5.1 Classical pulping processes

5.1.1 Soda pulping

Soda pulping is the oldest pulping processes known and consists of subjecting raw materials, cut and conditioned, to a cooking process with a given concentration of sodium hydroxide, at a specific temperature and cooking time, depending on the quality of the pulp to be obtained (chemical or semi-chemical) and the characteristics of the raw materials used [1, 2, 6]. A recovery of reagents and purification of black liquors is finally carried out. Each of these sections of the process can group together different operations. Thus, for example, in the preparation of the raw material, a debarking is carried out in the case of woody plants or pith is removed in the case of some vegetables (e.g. sunflower stalks), a cutting or reduction in size to produce chips or flakes, a cleaning to remove impurities, and so on. In the pulping section, the operations of impregnation of the raw material, cooking or delignification to separate lignin, washing of the solid fraction resulting from cooking and draining of the same to eliminate the fluid used in the washing can be integrated. In the same way, the sections of reagents recovery and purification of residual black liquors are made up of different operations.

Soda pulps have been obtained from different alternative raw materials, specially agriculture residues such as wheat straw [31], sunflower stalks [32, 33], vine shoots [34], olive tree pruning [35], sorghum stalks [36, 37], tagasaste [24], EFB [20, 38], *H. funifera* [39] and rice straw [29, 38, 40], obtaining different yields depending on the conditions of soda concentration, temperature and cooking time used. Soda pulping has also been carried out using additives such as anthraquinone and parabenzoquinone, which accelerate the delignification process and stabilize carbohydrates, improving the yield of the process with respect to the conventional "soda" process when operated under the same working conditions. Assays have been carried out using wheat straw, olive tree pruning, rice straw and EFB. For rice straw and EFB, pulps have also been obtained using KOH in aqueous solutions [20, 40].

Miao et al. [22] also analysed the composition of the hemp root bast (HRT) to further subject it to a process of soda pulping and bleach it with an elemental chlorine free (ECF) bleaching sequence. These authors conclude that HRT is a suitable raw material to make paper obtaining a pulp with high viscosity and brightness (893 mL/g and 85.52% ISO, respectively). González et al. and Marrakchi et al. [41, 42] also applied soda pulping to orange tree wood and *Stipa tenacissima* stems, respectively. The first ones studied the influence of operational variables in both pulping and pulp beating (temperature, 155–185°C; time, 40–90 min; soda concentration, 10–16%; and number of PFI beating revolutions, 0 to 3000) on the yield and on the pulp refining degree as well as the physical properties of resulting paper sheets. These authors found an optimum compromise as regards operating conditions (170°C, 40 min, 13% soda concentration and 2700 number of PFI beating revolutions), obtaining a pulp with tensile index, burst index and tear index of around 59.11 Nm/g, 4.10 kN/g and 2.79 mNm^2/g, respectively; these values deviate from their maximum values in 5.8, 2.2, and 1.4%, respectively. The pulp yield under these operating conditions is 43.9%; the refining degree is of 39.5°SR with the advantage of an increased drainability in paper production. These conditions involve a lower temperature, time, soda concentration and refining than those required to maximize the studied paper properties; so it is possible to save energy, chemicals and capital for industrial facilities. On the other hand, Marrakchi et al. [42] analysed the composition and fibre characteristics of the *S. tenacissima* steams and of its corresponding soda unbleached and bleached pulps. They conclude that the properties of *S. tenacissima* fibers are intermediate between those of non-wood and wood plants and are most often close to those of eucalyptus fibers. After studying a refining process and characterizing paper sheets obtained, these authors demonstrate the high potentiality of this non-wood species for papermaking applications.

5.1.2 Kraft pulping

The pulp obtained by this procedure is usually called Kraft (strong) if used for raw papers or "sulphate" if they are going to receive a further bleaching, although both denominations are used indistinctly. The name "sulphate" is due to the fact that it is the sodium sulphate, and not the sodium sulphide, the reagent that is replaced, although the real agent that acts during the reaction is the sulphide that is generated in the recovery treatment of residual black liquors [1, 2, 6]. The process can be divided into two parts: the first is the obtaining of the pulp, and the second is the recovery of the chemical reagents used from black liquors.

According to different authors [1, 2, 6], Kraft pulping process consists of the following stages:

i. The chips are taken to the reactor where they are cooked with white liquor (dissolution of sodium hydroxide and sodium sulphide), controlling the "liquid/solid" ratio.

ii. Pulping takes place during the established time, under appropriate pressure conditions.

iii. The black or residual liquor and the pulp are separated by filtration. The pulp is washed, and the black liquor is sent to the reagent recovery phase.

iv. Once washed, the pulp goes to the bleaching stage or to the raw paper manufacturing plant.

In the reagent recovery phase, organic compounds dissolved in black liquor are used to produce energy, thus reducing the rate of polluting effluents. The stages of recovery are as follows: (i) concentration of the black liquor in the evaporators; (ii) spraying of the concentrated black liquor in the oven, where the carbon reduces the sodium sulphate to sodium sulphide; (iii) the melted solids are discharged and dissolved in water, resulting in the green liquors; and (iv) the green liquor is sent to the causticizing stage, where the sodium carbonate reacts with the calcium oxide to form sodium hydroxide [1, 2, 6].

Some studies have been carried out to obtain Kraft pulps using alternative materials to traditional wood, including olive tree wood [43], *Cynara cardunculuns* L. [44], vine shoots [34], wheat straw [45] and kenaf [46]. Nevertheless, due to the more accessible structure of these materials compared to conventional wood materials, a soda process is usually applied to them, as this process is less pollutant. Thus, as an example, a factorial design of central composition experiments to find equations that relate the characteristics of the pulp and paper sheets with the operation variables have been realized using olive tree pruning [47, 48]. From these studies, it can be concluded that, in order to obtain pulp with suitable characteristics to be bleached to obtain paper and with good mechanical properties in the paper sheets, it is necessary to operate with an active alkali concentration of 25%, at 175°C during 90 min. The paper sheets obtained from olive tree pruning pulps were produced in different degrees of refining and were characterized attending their stretch index, burst index, and tear index. All paper sheets reach between 33 and 39 kN m/kg in the stretch index, between 1.5 and 2 kN/g in the burst index and 0.7–2.5 N m^2/g in tear index and not using a high refining degree (<45°SR) [47, 48].

5.1.3 Sulfite pulping

Sulfite pulps are obtained by cooking the lignocellulosic material with a solution of bisulfite and sulfur dioxide [1, 2, 6]. The cooking liquor is obtained by burning sulfur to obtain sulfur dioxide which is absorbed in a base of calcium, magnesium, sodium or ammonium. The most important variables of the "sulfite" process includes impregnation of the chips with the cooking reagents, dimensions and quality of the chips, temperature, time, pressure, pH of the white liquor, concentrations of sulfur dioxide combined (total and free), "liquid/solid" ratio and raw material used. Several "sulfite" processes have been proposed, including acid sulphite, bisulphite, alkaline sulphite, multistage sulphite, high-yield sulphite, etc., to obtain dissolving pulp [1, 2, 6]. In addition to these variables, it has been proposed to use molybdate or anthraquinone as catalysts, achieving a stabilization of the polysaccharides and an acceleration in delignification.

The sulfite process has been studied for several alternative raw materials but not as much as the soda and Kraft processes. Then, different studies of sulfite process with olive tree [35, 49], sunflower stalk [50], bagasse [51] and wheat straw [52] have been reported.

5.1.4 Organosolv pulping

These processes are characterized by the fact that the separation of lignin from lignocellulosic materials is achieved by solubilization with organic solvents, which are subsequently recovered for a new pulping cycle, resulting in a concentrate rich in lignin, from which different by-products can be obtained [53]. Among organic solvents used, alcohols (ethanol, methanol, butanol, etc.) and organic acids (acetic and formic acids) are commonly employed for non-woody materials [1, 2, 18, 24, 34, 54–66]. Nevertheless, acetone and other solvents such as phenol, formaldehyde, ethanolamine, ethylene glycol and ethanol-water have also been used for these alternative raw materials [1, 2, 19, 23, 34, 38, 60, 67–71], demonstrating that these materials can be used for the manufacture of pulp and paper through different processes with acceptable characteristics.

5.1.4.1 Pulping using alcohols

These are the most widely used processes due to the selectivity that these solvents contribute to the separation of the lignin and their easy recovery by distillation. In the case of the ethanol process, the influence of the operating variables (ethanol concentration, temperature, time and liquid/solid ratio) on the characteristics of the pulp and paper sheets obtained from different alternative raw materials, including olive tree [62], wheat straw [1, 2, 18], tagasaste [24, 57], sunflower stalk and *P. fortunei* [54, 55] and vine shoots [34], has been studied. As an example, in the case of wheat straw, when pulping is carried out at 200°C, with an ethanol concentration of 75% for 60 min, acceptable good values are obtained for yield (37.6%), holocellulose (88.8%), α-cellulose (46.9%) and lignin (7.2%) [1, 2, 18]. Methanol and butanol have also been used on wheat straw [37, 61].

5.1.4.2 Pulping using organics acids

Along with the processes that use alcohols, the processes that use organic acids are the following most used. The most common are those that use acetic acid and formic acid, and different studies have been reported with EFB [58], rice straw [63], jute [66], rapeseed straw [56], cardoon stalk [64], and wheat straw [65].

The pulping of wheat straw with acetic acid and formic acid has been carried out, studying the influence of operation variables on the properties of the resulting pulps. Comparing the results obtained when operating for times ranging between 0.5 and 2 h, at temperatures of 75–125°C and 150–200°C, and with concentrations of 50–100% and 50–80% of the formic and acetic acids, respectively, it is concluded that to obtain pulp with acceptable holocellulose (88.2%), α-cellulose (40.2%) and lignin (6.4%) contents are more effective than formic acid, operating at 50% concentration, 100°C and 2 h. This fact is mainly due to it requiring less acid and lower working temperature, with the consequent savings in chemical reagents and energy for heating [65].

5.1.4.3 Acetone process

Several studies have been studied with acetone solvent mainly on wheat straw [1, 2, 19, 60, 67]. From these studies it is concluded that it must be operated at 200°C, for 95–100 min and with 55–60% of acetone to obtain high holocellulose and α-cellulose values and low lignin and extractives, although the yield of the pulp is low [60]. To obtain good values of breaking length (3456 m), elongation (1.42%), burst index (1.36 KN/g) and tear index (3.86 mNm^2/g) of the paper sheets formed, a temperature of 200°C has to be used. On the other hand, if the brightness has to be high, it has to be operated at 140°C for 1 h with a concentration of 60% acetone [65].

6. Refining of cellulosic pulps

The refining of pulp is an operation that modifies, through the action of mechanical work and in the presence of an aqueous medium, the morphology of the fibres and their physicochemical structure, decisively changing the properties of the paper sheets obtained from the refined pulp [1, 2, 6]. Using a Sprout-Bauer refiner, the influence of refining pulp from different agricultural residues (wheat straw, sunflower stems, vine shoots, olive tree pruning, cotton stems and sorghum stems) on the corresponding pulp and paper sheets was studied [1, 2, 19, 32, 69]. In view of the results, it can be concluded that olive tree pruning pulp must be severely refined to obtain good quality paper, although the maximum values of the ring crush test (RCT) and the tear index are reached for refining grades of 45 and 55°SR, respectively. In the case of EFB soda-anthraquinone pulp, a study has been carried out in a PFI refiner, studying the influence of the cooking variables (soda concentration, temperature and time) and the number of turns in the PFI on the properties of the resulting paper sheets [20]. From this study it is deduced that under some operation conditions, 15% of soda, 170°C, 70 min and 2,400 turns in the PFI, the properties of paper sheets obtained deviate less than 12% from their optimum values (59.6 Nm/g for the traction index, 4.48% for elongation, 4.17 kN/g for the burst index and 7.20 mNm^2/g for the tear index), for a degree of refining of 47.5°SR, acceptable for the formation of paper sheets. Under these conditions, reagents, energy and immobilized capital are saved with respect to the maximum values of the operating variables used [20].

7. Bleaching of cellulosic pulps

The bleaching of cellulosic pulps is carried out for the elimination and/or modification of some constituents that add color to the raw pulp, generally using chemical reagents in one or more stages and trying to degrade the cellulose fibers as little as possible [1, 2, 6]. The main light-absorbing substances in the pulps are lignin and resins, so in order to bleach a pulp, these substances must be chemically transformed into a solid state in order to reduce their light absorption characteristics or be oxidized, reduced or hydrolysed, to make them soluble in aqueous solutions and thus be able to be removed from the pulps.

The need to reduce pollution from bleached pulp mills has led to the study of new bleaching sequences [1, 2, 6], with research focusing in three main directions: (i) bleaching processes with reagents without elemental chlorine (ECF), which consist of the total substitution of chlorinated stages by compounds such as chlorine dioxide (without elemental chlorine), regardless of whether other bleaching agents totally free of chlorine, such as oxygen, hydrogen peroxide, etc., are also used; (ii) bleaching processes with totally chlorine free reagents (TCF), using reagents such as oxygen, hydrogen peroxide and ozone, mainly [72]; and (iii) biological bleaching processes involving microorganisms or enzymes produced by them.

ECF and TCF bleaching processes including enzymatic stages have been studied for different alternative raw materials. It is worth highlighting the TCF processes which have been studied using different chemical reagents individually (hydrogen peroxide, oxygen, ozone, sodium perborate and peracetic acid) or with OZP bleaching sequences (where Z is an ozone stage) [1, 2, 6].

Hydrogen peroxide has been used for the bleaching of Kraft olive tree pruning pulp with a Kappa index of 21, operating at a temperature of 70°C and a consistency of 10%, and following a factorial design of experiments in which the peroxide concentration varies from 1 to 5% and the time from 30 to 210 min, finding that it is recommended to use a low-medium concentration of peroxide (1–3%) and a long time (210 min) [73]. Comparing the results with those of bleached pulps with other reagents, it is concluded that the viscosity of the pulps is higher in the case of peroxide bleached pulps than those bleached with oxygen, ozone or chlorine dioxide. To improve the Kappa index and brightness values of peroxide bleached pulp, it is desirable to combine hydrogen peroxide with oxygen or to use the combination oxygen and ozone [74].

For the bleaching of abaca soda pulp with peracetic acid [75], the influence of the operating conditions on the Kappa index, viscosity and brightness of the pulp and on the breaking length and burst index of the paper sheets was studied. Following a factorial design of experiments, it is concluded that operating at 55°C, with 4.5% peracetic acid for 150 min, a brightness of 79.9% is obtained (only 6.5% lower than the maximum possible) and the maximum possible values for the breaking length (6547 m), burst index (5.0 kN/g) and viscosity (1519 mL/g).

Peracetic acid has also been considered in the bleaching of olive tree pruning, finding that it has to be operated at 55°C for 90 min, a consistency of 10% and an acid concentration of 2.5%, providing good values for brightness and Kappa index and improving the viscosity of the bleached pulp with respect to crude pulp [76].

In the bleaching of abaca soda pulp with sodium perborate [77], the influence of the concentration of reagent (1–5%), temperature (60–80°C) and time (1–2 h) on the characteristics of the bleached pulp and the resulting paper sheets has been studied. It is concluded that in order to obtain pulp with the highest possible values of viscosity (1601 mL/g) and breaking length (5943 m), it is necessary to operate at 60°C, 1% perborate and 60 min, achieving a brightness of 62.7%, only 11.9% below the maximum possible.

For abaca soda pulp, the bleaching processes using hydrogen peroxide, peracetic acid, sodium perborate and the OZP sequence were compared from the point of view of pulp yield and brightness, breaking length and burst and tear indexes of the paper sheets. Overall, the best results are achieved for peracetic bleached pulp (4.5%, at 55°C for 0.5 h), providing little loss of yield (<1%) and some values for breaking length (6.555 m), burst index (4.97 kN/g) and tear index (15.77 mNm^2/g), which only decrease, with respect to those of the raw starting pulps, by 7.0, 8.8 and 20.9%, respectively, while brightness (77.4%) increases by 56.7%; with the additional advantage that by operating at a lower temperature and for less time than in the other bleaching processes considered, energy savings are produced for heating and immobilized capital for industrial installations. The pulp bleached with the OZP sequence has more brightness but loses more yield. Moreover, the characteristics of the paper sheets are worse, and the process requires higher costs of reagent, energy and immobilization [78].

The OZP sequence has been applied to EFB soda-anthraquinone and diethanolamine pulps [79]. For similar Kappa index values for the two pulps (14.2 and 17.3), the paper sheets of the raw soda-anthraquinone pulp exhibit higher values for tensile (25.8 Nm/g), elongation (2.35%), burst index (1.69 kN/g) and tear index (0.50 mNm^2/g) and brightness (60.6%) than the diethanolamine pulp, but the latter has a higher viscosity (659 mL/g). When OZP bleaching sequence is used, the diethanolamine pulp exhibits higher viscosity (783 mL/g), and the properties of the paper sheets are similar to or better than those of the soda-anthraquinone pulp: 22.2 as opposed to 20.4 Nm/g for the tensile index, 1.30 vs. 1.42 kN/g for the burst index, 0.71 vs. 0.70 mNm^2/g for the tear index and 71.3 vs. 77.5% for brightness [79].

7.1 Biobleaching

It is worth highlighting in this section that apart from xylanases, the use of laccases has been used for the bleaching of alternative raw materials [80–84]. As it is known, these enzymes need a mediator to make the bleaching more effective since thanks to them they are able to oxidize not only the phenolic part but also the non-phenolic of the lignin.

The work of Camarero et al. [80], who apply three different fungal laccases (from *Pycnoporus cinnabarinus*, *Trametes versicolor* and *Pleurotus eryngii*) and two mediators, 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 1-hydroxybenzotriazole (HBT) to bleach flax pulp using a TCF sequence (enzymatic stage (L) plus hydrogen peroxide bleaching (P)), is noteworthy. These authors obtain delignification values of up to 90% after hydrogen peroxide bleaching when initial pulp is subjected to the enzymatic pretreatment (L). These results are improved when they apply a P stage under pressurized oxygen, obtaining a pulp with 82% ISO of brightness, and kappa index close to 1. Fillat et al. [81] also bleached flax pulp using natural mediators: syringaldehyde (SA), acetosyringone (AS) and p-coumaric acid (PCA) in combination with the laccase of *P. cinnabarinus* as a pretreatment prior to hydrogen peroxide bleaching stage. All mediators decrease the kappa index and increase the brightness of the bleached pulps after peroxide bleaching especially when SA was used. On the other hand, soda-anthraquinone pulp from orange tree pruning is also bleached by Fillat et al. [82]. In this case three different laccase-mediator systems (LMS) were used as pretreatment to an alkaline extraction plus a hydrogen peroxide bleaching: laccase from *Trametes villosa* (Tv), either in combination with 1-hydroxybenzotriazole (HBT) or with acetosyringone (AS) as natural mediator, and laccase from *Myceliophthora thermophila* (Mt) in combination with AS. The three laccase-mediator systems improve the bleaching sequence, with L-Tv + AS being the LMS that provides the highest delignification and improvement of optical properties. Finally, Martín-Sampedro et al. [83] also bleached soda pulp from olive tree pruning using not only a typical LMS but also adding xylanase jointly or prior to LMS to study the effect of this enzyme on the characteristics of the bleached pulps. The best results are found when both enzymes are applied in the same stage. In these conditions the lowest hydrogen peroxide consumption (63%), kappa index of 11.6 and brightness of 46% ISO are reached. Same authors [84] also bleached pulp from oil palm empty fruit bunches using laccase and xylanase. An enzymatic process with xylanase (X) and/or laccase (L) was incorporated before the alkaline extraction step

(E) and the hydrogen peroxide bleaching (P). Comparing with controls, the LEP sequence results in an improvement of optical properties (colorimetric properties and brightness) and a reduction of the kappa index. When both enzymes (xylanase and laccase) are used jointly, no improvement is detected; however, when the xylanase stage is applied before the laccase stage, the beneficial effects of laccase are boosted. Thus, the XLEP bleached pulp shows a brightness of 60.5% ISO, a kappa index of 5.4 although the hydrogen peroxide consumption increase (77.0 vs. 64.5% and 73.8% for EP and LEP, respectively).

8. Integration of the pulp and paper industry using alternative raw materials into the biorefinery concept

The concept of lignocellulosic biorefinery aims at the integral use of the main components of lignocellulosic raw materials to obtain energy, chemicals and products [85]. The pulp and paper industry is an excellent initial point for the establishment of this concept as it has the best infrastructure for biomass fractionation and conversion and a great deal of practical industrial experience. Then, the classical pulp and paper industry, including Kraft, sulfite and soda technologies, has been applying this concept for a long time as it not only produces paper as the main product (cellulosic fraction) but also recovers the reagents and produces energy from the residual black liquors (lignin-rich fraction) as well as the generation of bioproducts such as tall oils, which are sold to obtain high added value products (e.g. adhesives, detergents, etc.), and lignin for the production of chemicals or materials. In the future, the extraction of hemicelluloses prior to pulping will be included in order to make maximum use of lignocellulosic materials. A general scheme, which will be developed below including also gasification of lignin, is shown in **Figure 1**.

Using the same scheme-work of the pulp and paper industry with classical pulping methods, different organosolv pulping processes have been developed to produce cellulosic pulp and other products from different alternative raw materials such as agriculture residues [53], among them, those employing ethanol such as the Alcell© process for the production of cellulosic pulp, giving value to other biomass fractions, such as high-quality lignin in the residual black liquor with several potential industrial applications, and the Lignol© process, which also extracts lignin, as well as sugars for the production of ethanol, oligomers, furfural and acetic acid. However, one of the disadvantages of these processes lies in the incorporation of both extracts and a part of the hemicelluloses to the residual black liquors. For this reason, the possibility of carrying out a hydrolysis pretreatment of the polysaccharides with the original raw materials prior to organosolv pulping methods, using water at a high temperature (hydrothermal treatment), has been explored [53]. Then, a hydrolysis of the acetyl groups to acetic acid is produced, which acts as a catalyst solubilizing all or part of the hemicelluloses (autohydrolysis) and then resulting in a pretreatment aqueous fraction with oligomers (mainly gluco-oligosacharides and xylo-oligosacharides), sugars (glucose, xylose, arabinose), acetic, furfural or 5-hydroxymethyl-2-furfural (HMF) and some lignin. Oligomers are used as food additives or substrate for sugars, after hydrolysis and fermentation (xylose and arabinose could be fermented to ethanol or xylitol); and furfural and lignin derivatives have applications in the chemical industry [86, 87]. The disadvantage of this fractionation is the low selectivity towards cellulose, giving rise to a solid fraction structurally affected, which can limit its later use; but an adequate hydrothermal pretreatment achieves a solid fraction that can be used to obtain pulp and paper by classical or organosolv procedures, whose resistance can be improved using a relevant refining.

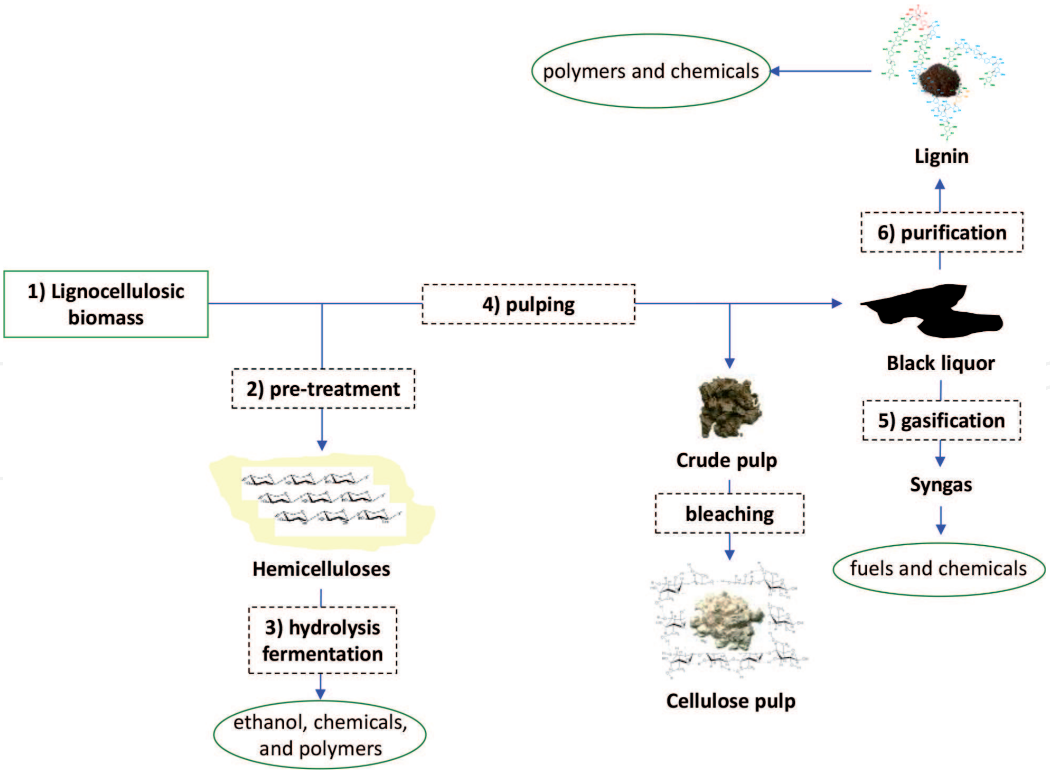

Figure 1.
Scheme of integration of pulp and paper industry into the biorefinery concept in the future.

In the pulping processes of the solid fraction coming from autohydrolysis or hydrothermal pretreatment, some residual black liquors are obtained, with lignin being the majority component. These liquors, after the separation of water and/or organic solvents used in cooking (which are recycled in the cooking process), are transformed into a concentrate rich in lignin. From these concentrates lignin can be obtained for different uses, and/or it can be subjected to gasification processes with the aim of obtaining high-quality products such as hydrogen, methanol, synthesis gas or dimethyl ether (DME) for motor applications [86–89].

8.1 Hemicellulose isolation by hydrothermal treatments

As commented above, one of the possibilities to convert the classical chemical pulp and paper industry into a biorefinery is to extract a portion of hemicelluloses from lignocellulosic materials prior to pulping, obtaining a liquid fraction enriched in hemicellulosic carbohydrates that can be converted into ethanol and/or chemical products. One of the options for the separation of hemicellulose from lignocellulosic materials is its depolymerization by autohydrolysis, also known as hydrothermal process, which does not require the addition of acids as it is auto-generated in the process [53, 85]. In addition to the process of autohydrolysis itself, the process of steam explosion is very significant (once autohydrolysis has taken place, the mixture undergoes a sudden decompression to produce the vaporization of the water contained in the fibers and the consequent disaggregation of the lignocellulosic matrix), as well as its variants, such as the Rash, Masonite, Iotech, Siropulper and Stake processes [53, 85].

These hydrothermal treatments can be carried out in a very wide range of operating conditions, with the temperature, time, solid concentration and particle size of lignocellulosic materials being the most influential variables [85]. In the case of autohydrolysis, the range of temperatures to treat lignocellulosic materials in an aqueous medium is in the range between 150 and 250°C. Under these conditions, the self-ionization of water generates protons that act as a catalyst for the hydrolysis of the hemicellulose, reacting among others the acetyl groups (present in the form of esters in the hemicellulosic heteropolymers), which are released in the form of acetic acid. Its contribution to the generation of protons is 1700 to 1,000,000 times greater than that of water, so the contribution of aqueous protons to the hydrothermal process can be neglected once acetic acid has been generated. At the same time, there is total or partial solubilization of hemicelluloses and their conversion with good yields of oligosaccharides and monosaccharides, which can be used for different purposes [53, 85].

Other minor reactions associated with this type of process are the formation of products such as furfural from pentoses and HMF from hexoses; the generation of carbon dioxide by decomposition of carboxyl groups present in uronic acids; the condensation of some unstable molecules that intervene as reaction intermediates; the decomposition under severe conditions of products such as furfural, sensitive to acid concentration; the decomposition of HMF to formic and levulinic acids; and condensation reactions with lignin [90].

Different studies with traditional woody materials such as eucalypt have shown a pre-extraction of hemicellulose prior to pulping process by hydrothermal processes [91–93]. In the same way, these hydrothermal processes have also been applied to alternative raw materials such as paulownia [55], sunflower stems [54], rice straw [71], tagasaste [25] and *H. funifera* [94].

The influence of the temperature (160–200°C) of the autohydrolysis process applied to paulownia on the composition of the resulting solid and liquid fractions has been studied [55]. It is found that the maximum concentrations of glucose, xylose, arabinose, acetic acid, furfural, HMF and oligomers of the resulting liquid fraction correspond to when operating at maximum temperature.

A similar study carried out with sunflower stems concludes that at 190°C the highest values are obtained for the glucose, xylose and arabinose contents of the liquid fraction of the hydrothermal treatment, with a yield of 24.5%, while the yield of the solid fraction, which can be pulping, is 72.5% [54].

In the case of rice straw, the influence of temperature (150–190°C), time (0 to 20 min after reaching the working temperature) and liquid/solid ratio (6:10) on the hydrothermal treatment, on the lignin content, on the yield of the resulting solid fraction and on the composition of the corresponding liquid phase (glucose, xylose, arabinose and acetic acid) was studied [71]. It follows that in order to obtain high values of glucose (1.92 g/L), xylose (3.97 g/L), arabinose (0.99 g/L) and acetic acid (1.96 g/L) concentrations, it is necessary to operate at high temperature (190°C) and low-medium conditions for time (15 min) and hydromodule (9), which allows capital savings by not operating with the maximum time and using the maximum hydromodule value. The yield obtained for the solid fraction is 88.1%, and the lignin content is 24.43%.

Finally, tagasaste wood was submitted to hydrothermal treatment at 175–185°C [25]. Then, a liquor containing a substantially increased amount of oligomers (between 16.6 and 47.7% as percentages with respect to the content of the raw material in each polymer fraction) is obtained. In the case of *H. funifera*, a sulphuric acid-catalysed hydrothermal treatment (170°C, 0, 20 min after reaching operating temperature, 8 liquid/solid ratio, and 0.3% sulphuric acid), gives a liquid fraction containing 4.62% of glucose, 10.56% of xylose, 1.28% of arabinose, and a solid fraction with a solid yield of 57.0%.

8.2 Pulping of the solid fraction from hydrothermal treatment

Hydrothermal treatments under relatively mild operating conditions (temperature and time) do not cause significant alterations in the cellulose. In this way, solid fractions susceptible to delignification or pulping are obtained [53].

The solid fraction of the hydrothermal treatment of paulownia carried out at 190°C was subjected to pulping process with ethanol following a factorial design of experiments [55]. The conclusion of this work is that operating at 180°C for 30 min and an ethanol concentration of 20%, obtained pulp has acceptable values of Kappa index and viscosity, and their corresponding paper sheets have a brightness of 27.4% ISO, a tensile index of 28.87 Nm/g, a burst index of 1.22 kPam^2/g and a tear index of 1.23 kNm^2/g.

In the case of sunflower stems [54], the solid fraction of a treatment carried out at 180°C is cooked with ethanol (70%, 170°C for 2 h and a hydromodule of 8) giving rise to a pulp with properties (36.3% of pulp yield, 69.1% cellulose, 12.6% hemicellulose, 18.2% lignin, 551 mL/g viscosity, 3.8 km breaking length, 1.23% elongation, 1.15 kN/g burst index and 2.04 mNm^2/g tear index) similar to that obtained by the soda process.

The influence of operating conditions (temperature from 160 to 180°C, time from 30 to 90 min and concentration of diethanolamine from 60 to 80%) on the pulping process of the solid fraction obtained from a hydrothermal treatment of rice straw (carried out at 190°C) on the characteristics of the pulp (yield, Kappa index, viscosity and degree of refining) and of the paper sheets obtained from them (length of rupture, elongation, burst index, tear index and brightness) was also studied [71]. It is deduced that it is convenient to operate at 162.5°C, 60 min and 70% of diethanolamine, since paper sheets present characteristics that deviate little from the optimal ones (less than 8% in the worst case), saving chemical reagents, energy for heating and immobilized capital for the installation, when operating with values of time and the concentration of diethanolamine medium and medium-low temperature, with respect to the maximums considered; likewise the values found for the yield and Kappa index deviate less than 14% with respect to the optimal values.

Autohydrolysed tagasaste wood was also submitted to ethanol and soda pulping procedures [25]. The autohydrolysis prior to ethanol pulping increases yields (53–60%); reduces Kappa index (28.8–34.6), but also viscosity (755–857 mL/g); and decreases paper strength (2.97–5.22 kNm/kg). However, applying a refining process to tagasaste pulp is found to improve its strength-related properties more markedly than in soda pulp from the same material (tensile index of 44 kNm/kg). In the case of *H. funifera*, the samples pretreated with sulphuric acid-catalysed autohydrolysis was subsequently submitted to soda, soda-anthraquinone, ethanolamine, ethylene glycol, diethanolamine and diethyleneglycol [94]. In this case, the best pulp of *H. funifera* pulp is obtained by cooking with 10% NaOH and 1% anthraquinone at 155°C for 30 min, exhibiting good values of yield (48.3%), viscosity (737 mL/g), Kappa index (15.2), tensile index (83.6 Nm/g), stretch (3.8%), burst index (7.34 kN/g) and tear index (3.20 mNm^2/g). Moreover, the soda-anthraquinone pulps of raw material have better properties than the pulps from solid fraction of hydrothermal treatments.

8.3 Use of residual liquors components obtained during pulping

The valorization of lignin-rich black liquors generated from pulping processes is another transition path from the traditional pulp and paper industry to future biorefineries. Generally, residual lignins from black liquors are used to obtain energy for processing plants, mainly by combustion. However, the aromatic structure of lignin makes it a potential source for the production of new bio-based high-value products and chemicals, increasing the sustainability and competitiveness of this pulp and paper industry [86]. Other different fractions of lignin and compounds such as various polysaccharides present in these black liquors, which may not have specific applications or their transformation into high value-added products may not be profitable, can also be valorized by gasification process [89].

Pulp and paper industry is estimated that moves around 70 million tonnes of lignin annually [95], of which only just over 1 million tonnes are currently marketed, corresponding to lignosulfonates, and which have an established market for use in various uses such as plasticizers and dispersion agents, whereas Kraft lignins are used in the recovery tanks of products from the paper plants themselves and only market around 100.000 tonnes per year. Finally, only a few hundred tonnes of lignins from the soda process come onto the market each year, although this quantity is expected to rise rapidly to around 10,000 tonnes due to the fact that an increasing number of small paper mills, which use agricultural waste and non-wood species to produce cellulose, are introducing lignin recovery processes as the only way to meet environmental effluent treatment specifications.

8.3.1 Lignin applications

Depending on the biomass feedstock, pulping technology and conditions and isolation procedures, lignin has distinct features that may render them useful for different applications. Purity, molar mass and chemical functionalities are some of the characteristics to take into account [96]. So, a detailed knowledge of lignin structure, composition and purity is required in order to determine its behaviour in different potential applications. In this sense, characterization of residual lignins from Kraft and soda-anthraquinone pulping of agriculture residues such as olive tree pruning [97] and wheat or barley straw [98], as well as vegetables like *L. leucocephala*, *C. proliferus*, and *H. funifera* [99, 100], has been carried out.

Among the different characteristics of lignin, its high heterogeneity is one of the most important, which not only affects its structure but also its high distribution of molecular weights (range from 1.000 to 300.000 Da for the same sample) [101]. Therefore, fractionation is one of the ways of obtaining reactive lignins. The preparation of lignin with a defined molecular weight distribution can be carried out by means of different processes: ultrafiltration, selective extraction with solvents and differential precipitation.

The technique of ultrafiltration and nanofiltration is one of the methods being investigated today, with the dual intention of on the one hand reducing the organic load contained in the digestion solution, for its subsequent reincorporation into the pulping process without the loss of inorganic reagents, and on the other obtaining valuable organic resources for use in the development of high-value-added materials. By means of ceramic membranes capable of filtering the residual liquor until the separation of substances smaller than 1 kDa, low molar lignin fractions (1000 g/mol maximum) are obtained. After suitable purification processes, these lignins have a high phenolic hydroxyl content (and/or acid groups), high reactivity and low processing and handling temperatures. In this way, Toledano et al. [102] propose ultrafiltration as a fractionation process to separate different molecular weight lignin fractions from olive tree pruning organosolv black liquor.

Solvent extraction of lignin can be carried out primarily in two ways. In one case, lignin is extracted by a single solvent or a sequential use of multiple solvents. In the other case, a solvent is used to dissolve lignin and then precipitated using chemical (mainly with acids) treatments. Then, Domínguez-Robles et al. [103] used different proportions of acetone (40 and 60%) in water for lignin fractionation of two different sources (organosolv and soda wheat straw lignins), obtaining different fractions with different molar masses and functional groups. Finally, fractionation of the lignins by differential precipitation consists of extracting different lignin samples as the pH of the solution is gradually lowered. It is the most commonly used method because the simple addition of a strong acid is sufficient, compared to the high costs of the other two methods. However, it has a disadvantage derived from the formation of colloids during precipitation, which can greatly complicate the filtration process. In this sense, Domínguez-Robles et al. [104] have proposed an acid precipitation of wheat straw lignin from soda black liquor using three different inorganic acids (phosphoric, sulphuric and chloride acids) at three different concentration levels, achieving pH values from 11 to 2.

Different lignin applications have been suggested depending on its properties. Then, poorly degraded lignin is employed as dispersants, surfactants and thermoplastic blends or copolymers [105–107] or as an aromatic compound platform to obtain fine chemicals such as polyols, benzene, xylene, toluene, vanillin, ferulic acid, etc. [87]. In contrast, extensively depolymerized lignin, therefore, with a high phenolic content, is suitable for coating, adhesives and composites [108–111]. In this sense, some examples of lignin valorization from alternative raw materials have been reported. Then, Borrero-López et al. [112] showed the possibility to produce olegels from soda lignin obtained from solid state fermented wheat straw; Tejado et al. [113] assayed soda-anthraquinone flax lignin and ethanol-water wild tamarind lignin to phenol-formaldehyde (PF) resin production; Domínguez-Robles et al. [103] investigated the use of soda wheat straw lignin as natural adhesive for the production of high-density fibre board; and Domínguez-Robles et al. [98] analysed Kraft, soda and organosolv wheat straw lignins as a binder material for electrodes in rechargeable lithium batteries.

8.3.2 Gasification of residual liquors components

Any proportion of the agricultural raw material non-suitable for pulp and paper production, in addition to lignin and other compounds such as various polysaccharides obtained in lignin separation processes, may be converted—via pyrolysis—into several types of fuels and petrochemical substitutes [1, 88].

As commented above, different fractions of lignin and other compounds such as various polysaccharides can be obtained in lignin separation processes. Some of these fractions may not have specific applications, or their transformation into high-value-added products may not be profitable, so they may be suitable for a gasification process [89]. This consists of the partial oxidation of the lignocellulosic residues to obtain carbon monoxide, hydrogen, methane, nitrogen and carbonic anhydride mainly, in proportions that depend on the raw material considered and the conditions of the process. Three types of processes can be distinguished: (i) exothermic, using oxygen or air to obtain carbon monoxide or a mixture of carbon monoxide and nitrogen (lean gas); (ii) endothermic, which use water vapor to obtain carbon monoxide and hydrogen (synthesis gas); and (iii) balanced or mixed, using oxygen and water vapor or air and water vapor to obtain carbon monoxide and hydrogen or a mixture of carbon monoxide, hydrogen and nitrogen.

Gasification gases can be used as fuels or to obtain chemicals. Among the latter, those obtained from carbon monoxide (methyl formate, formamide, formic acid, carbonyls, acrylic acid, etc.) and those obtained from carbon monoxide and hydrogen (ammonia, nitric acid, hydrazine, urea, hydrocyanic acid, aldehydes, explosives, etc.) can be distinguished. For example, pyrolysis of soda *H. funifera* lignin gives a gas mixture containing 1.13% H_2, 31.79% CO and 1.86% CH_4 by weight, whereas gasification of the same sample provides a mixture containing 0.18% H_2, 24.50% CO and 17.75% CH_4, also by weight [39].

9. Conclusions

The availability and concentration of wood in areas of easy access, the elevated fibre content, the cost of transport, the ease of storage as well as the stability of the raw material and its performance during the pulping process have supported the use of the wood in the pulp and paper industry. However, due to the numerous advantages of certain alternative raw materials (low-cost fibers, fast growth, low lignin content and fiber morphology, among others), they have proved to be a viable option as a starting raw material for the production of a wide range of different papers. On the other hand, taking into account the concept of lignocellulosic biorefinery, the pulp and paper industry is a good starting point since from its beginnings it not only produced pulp for paper but also energy. However, this industry needs different innovations to adapt even more to this concept. These innovations include the valorization of the extractives and hemicellulosic fractions through extraction prior to the pulping process, the valorization of black liquors through gasification or purification, the valorization of lignocellulosic waste through gasification or other processes such as saccharification and fermentation and also the introduction of new alternative raw materials to wood, as summarized in this work.

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Conflict of interest

The authors declare no conflict of interest.

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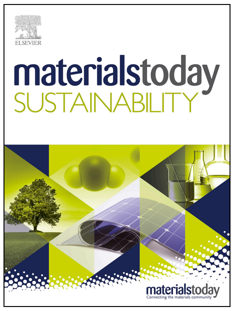

A Brief Overview of Renewable Plastics

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A Brief Overview of Renewable Plastics

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Abstract: Plastic waste has widely spread to almost every corner of the blue planet, imposing serious problems to the live organisms and the environment. Traditional plastics are derived from fossil feedstock and difficult to be degraded nature. To mitigate the carbon footprint and the impact on environment, renewable plastics that are both biobased and biodegradable are the future directions for the sustainable development of the plastic industries. In this mini-review, the current status, including the major commercial renewable plastics and the new generation of renewable plastics from ocean waste, will be briefly narrated.

1. Introduction

Plastics represent a group of organic polymers including synthetic, semi-synthetic or natural materials that are malleable and can be molded into solid objects. The first synthetic polymer Bakelite was formulated by a Belgian chemist Leo Baekeland in the 1900s [1], which symbolized the birth of the modern plastic industry. With the salient virtues of low-cost, lightweight, durable, odorless, versatile, etc., there was a large and rapid expansion of plastic manufacturing started in the 1950th. In 2015, the annual global production of plastics exceeded 300 million metric tons and is predicted to surpass 500 million metric tons by 2050. The plastic polymers are broadly applied in food packages, textiles, automobiles, electronics, etc., penetrating almost every aspect of daily life.

Companying the massive production, there is a lack of effective implements or strategies to deal with the disposal nor the recycling of the plastic waste. Plastic commodities often have relatively short use life (e.g. plastic bags of ~one year) but may preserve in the environment for centuries. The decomposition periods of general commodities are exemplified in Figure 1, and plastics are among the toughest ones to be decayed. Geyer *et al.* reported that the accumulative production of plastics reached 8.3 billion metric tons from the year 1950 to 2015, and 7.2% of them was recycled for secondary uses, 9.6% was incinerated which generated harmful gases into the atmosphere, while the majority was dumped into lands, rivers and seas (see Figure 2) [2]. The tremendous plastic debris, known as “white pollution” that are hard to be digested in nature, has become a critical environment threat to the ecological systems.

Especially, the plastics in ocean pose serious impacts on the marine lives and systems. Figure 3 shows the global distribution of plastics in oceans. The plastic waste has spread to a broad area, with apparent accumulations in the Pacific Ocean (as the so-called "Great Pacific Garbage Patch") [3]. Studies show that the plastic waste has exposed risks on more than 700 species of ocean animals as well as the coral reefs [4]. For example, emerging cases were reported that plastics were found in the stomachs of seabirds, the death of turtles entangled with plastics, etc. Besides, the detection of microplastics in food and in air samples have induced increasing concerns on their potential influences on human health [5-7].

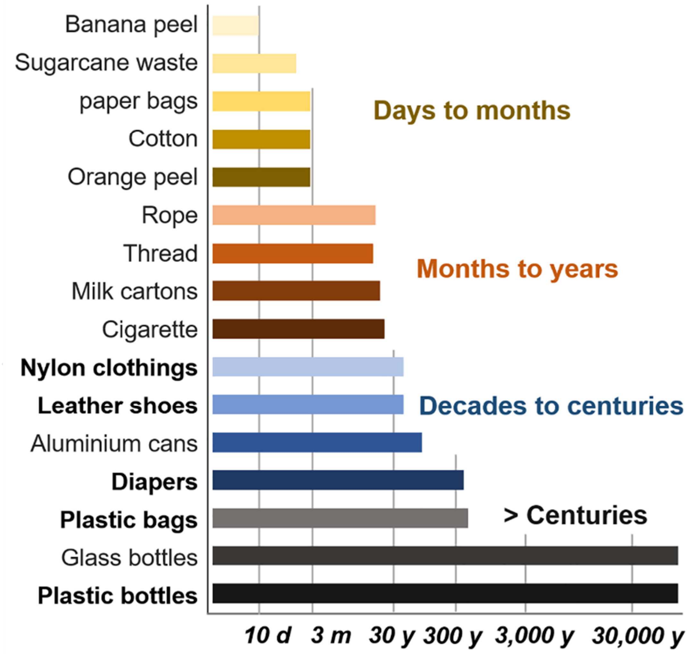

Figure 1 The average decomposition periods for various common commodities. "d" refers to day while "y" refers to year. The commodities marked in bold are the representative plastic waste.

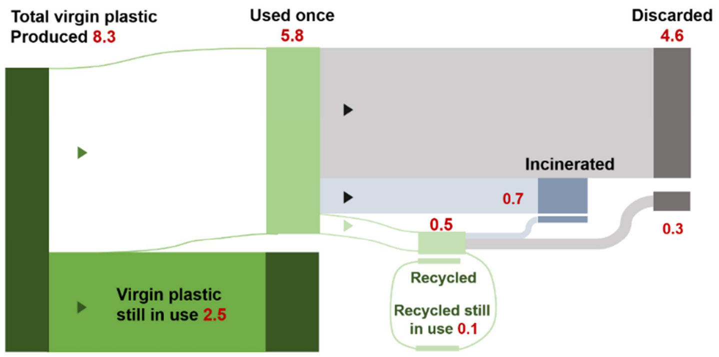

Figure 2 The fate of globally produced plastics (use, recycle and disposal) from 1950 to 2015. The unit of numbers is billion metric tons. Data from Ref 2 and the *Economist* magazine.

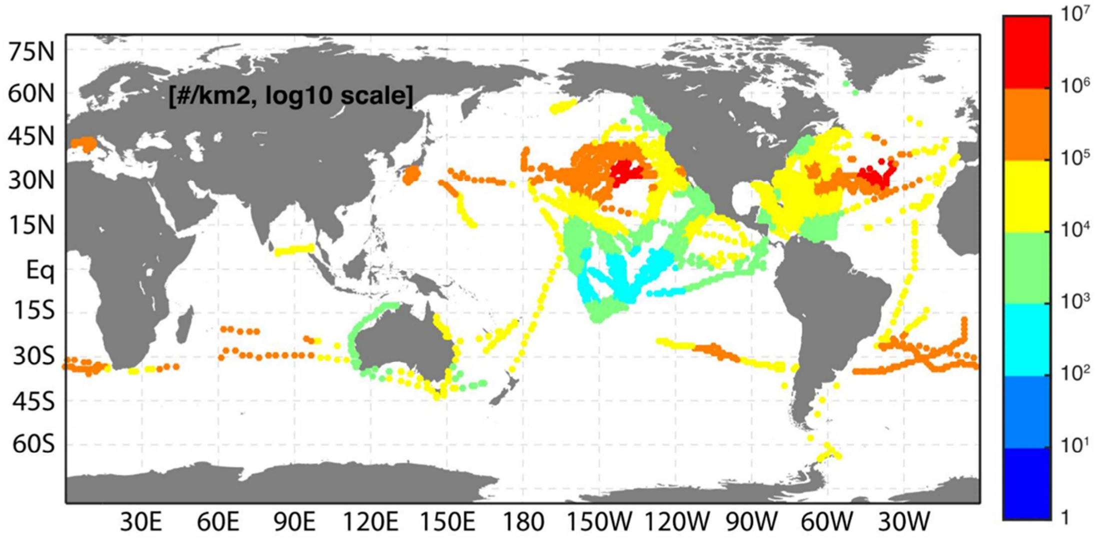

Figure 3 The particle count of plastic samples (collected) indicating the worldwide distribution of plastic waste. The data were standardized using a generalized additive model to represent no-wind conditions in the year 2014. Reprinted with permission from Ref 3 under the Creative Commons Attribution 3.0 Unported license (https://creativecommons.org/licenses/by/3.0/legalcode).

2. Classification of plastics

There are different ways to categorize plastics, based on the chemical structures, the resources and the properties. The two terms, biodegradable and biobased are associated with the sustainability of the plastic materials. The confusion of the two concepts often happens despite they have fundamentally distinct meanings. The so-called bioplastics in market refer to plastics that are either biobased or biodegradable, or both. Biodegradable describes the feasibility of a plastic to be decomposed by the biological microorganisms in natural environments (such as in soil, ocean, etc.), which is defined by the standard ISO/TC61/SC5/WG22 [8]. For ideal renewable plastics, the materials should be fully biodegraded into carbon dioxide (CO_2) and water with negligible residues. The degradation period of biodegradable plastics is normally much shorter than the traditional plastics, ranging from days to months. The environmental conditions affect the decomposition more significantly, instead of the species. For example, about 84% of polylactic acid (PLA) can be degraded in compost within two months while the biodegradability of PLA may be < 10% in soil after more than three months (data from *IBioIC*). The situations are similar for starch-based plastics.

In contrast, biobased plastics refers to the origin that the materials are derived from renewable resources such as biomass rather than fossil feedstock (fossil-based). The conversion of renewable biomass into useful chemical and materials are a broadly investigated field [9-15]. Since the resources are sustainable, the decompositions of biobased plastics in principle induce zero net carbon emission. Of note, biobased polymers are not necessarily biodegradable, and vice versa (see Figure 4a). For instance, the conventional plastic polyethylene (PE) can be synthesized from renewable resources *via* new technologies, which becomes biobased PE (or bio-PE) but is still non-biodegradable, whereas polycaprolactone (PCL) is a fossil-based, biodegradable plastic. As another example, corn lignin has been recently converted into terephthalic acid [16]. Should corn-derived terephthalic acid is further processed into polyethylene terephthalate (PET), the PET is only bio-based. To this end, plastics that are both biobased and biodegradable would have minimal environmental impacts [17] and are defined as the renewable plastics in this mini-review. A summative overview of the major commercial renewable plastics and emerging renewable plastics (from non-edible biomass and CO_2) was provided as Figure 5.

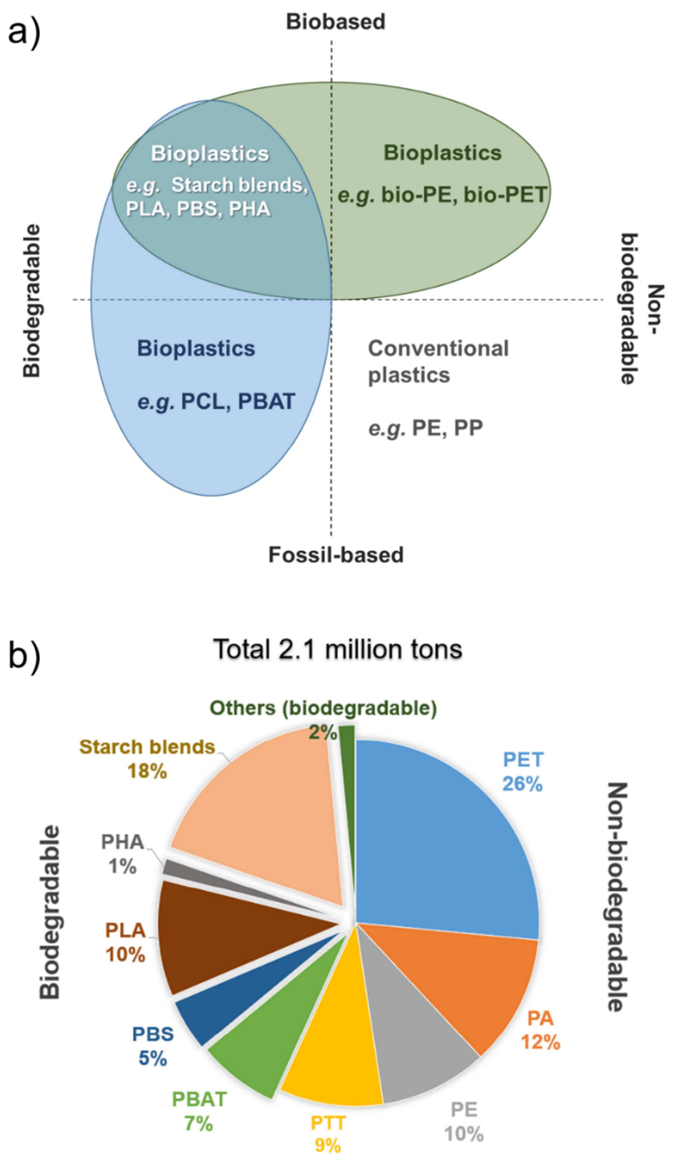

Figure 4 a) the classifications of plastics by the sustainability; b) The global production of bioplastics by material types. Data from *European Bioplastics*.

3. Commercial renewable plastics

The plastic industry at present still has a long distance from sustainable development. Most of the widely used plastic materials, e. g. PE, polypropylene (PP), polystyrene (PS), are fossil-based and non-degradable. According to the data provided by the *European Bioplastics*, the production of bioplastics was 2.1 million metric tons in 2018, which takes up < 1% of the total plastic market. Encouragingly, the demands for renewable plastics keeps growing these years despite of the low market share [18-20]. As shown in Figure 4b, the left parts (protruded) represent biodegradable plastics, most of which are derived from renewable resources except for polybutyrate adipate terephthalate (PBAT). The right-hand side displays biobased, non-biodegradable materials including PE, PET, polyamides (PA) and polytrimethylene terephthalate (PTT). Overall, for the renewable plastic (both biobased and biodegradable) market, polybutylene succinate (PBS) and polyhydroxyalkanoate (PHA) take up a small portion, while starch blends and PLA are the dominant types in the current market.

3.1 Starch blends

Starch blends have the largest production in the bioplastics market. Starch is an abundant, readily-available carbohydrate in plants comprised of the linear amylose polymer chains and the branched amylopectin chains. Thermoplastic starch can be generated by a process named gelatinization which happens upon heating in the presence of a plasticizer such as water, glycerol, etc. The properties of resultant thermoplastic starch rely on the operation parameters (e.g. time, temperature, composition, etc.). The producing cost for thermoplastic starch is almost the cheapest among renewable plastics, whereas pure starch has been rarely employed in real applications because of the low tolerance to moistures. Blending the starch with other polymers such as PLA, PBS, etc. offers a solution to the durability issue and constructs usable plastic composites with relatively lower prices.

3.2 PLA plastics

PLA is probably the most known renewable plastic with good biodegradability and biocompatibility. It is an aliphatic polyester constituted by the building block lactic acid, which can be produced by biological or chemical methods from cellulosic biomass such as starch, corn stalks, sugar canes, etc. [21]. Biological fermentation of glucose from corns is a relatively mature technology, and thus the production of PLA becomes easily available and relatively competitive in costs to the conventional polymers. The degradation rate of PLA depends on the properties of the final products and the disposal environment, but normally it takes half to two years for the PLA plastics to be degraded which is much shorter than the traditional fossil-based plastics [22].

The synthesis of PLA plastics are achieved by two methods: the condensation polymerization of lactic acid and the ring opening polymerization (ROP) of lactide. Direct polymerization of lactic acid usually leads to low molecular-weight (MW) PLAs due to the water residues generated during the reaction. A further step of chain coupling or the process azeotropically dehydrative polymerization are required to form high MW PLAs which are more suitable for practical applications. On the other hand, the lactide is a lactone cyclic dimer of lactic acid, and thus the ROP of lactide obviates the “water” issue leading to high MW PLA materials. Moreover, the building blocks (lactic acid or lactide) are chiral with D- and L-isomers, and the physicochemical and mechanical properties of PLA products can be regulated by the stereochemistry [23]. For example, when the proposition of D-lactic acid is beyond 20% in the starting monomers, amorphous PLA is more likely to form. Besides, the poly(L-lactic acid) (PLLA) constituted by pure L-lactic acid or the poly(D-lactic acid) (PDLA) by pure D-lactic acid are semi-crystalline with a melting temperature of 170~180 °C, but the equivalent mixtures of PLLA and PDLA will form a stereocomplex (racemic crystallite) leading to elevated melting temperature and enhanced mechanical strength. With various merits, PLA has been exploited in textiles, food packaging, and biomedical areas, and holds potentials to substitute conventional plastics such as PP, etc.

3.3 PBS plastics

PBS is an aliphatic polyester constituted by the succinic acid and 1,4-butanediol monomers. Traditionally, the monomers are synthesized from fossil feedstock, whereas new advancements have enabled the production of them from renewable biomass resources (sugars, etc.) mainly by biological method in industry scales. PBS possesses similar properties as PP, and has a better mechanical property and a wider processing window than PLA, with potential applications in textiles, automotive, sports devices, etc. Besides, adding fillers and/or fabricating PBS composites offer a way to further improve the properties to meet with the requirements of specific applications. However, the production costs for PBS are still relatively high and future developments are required to make it more economically viable.

3.4 PHA plastics

PHAs designate a sum of polyesters (approximately > 100 species) [24] that are industrially synthesized by biological fermentation of sugars such as glucose, which was first discovered by the French scientist Maurice Lemoigne in 1925. The commercialization of PHAs as a renewable plastic has been realized recently due to the progress in the production and purification technologies to reduce the prices. The polymer structures (the monomer, MW, etc.) of PHAs are adjustable by the bacteria strains, growth conditions, etc., and thus different PHAs boast various physicochemical properties. The poly-3-hydroxybutyrate (P3HB) is the most prevalent type of PHAs in industry followed by poly(3-hydroxybutyrate-co-3-hydroxyvalerate), which can be applied in packaging, fibers, etc. Pure PHAs are susceptible to temperature and shear during processing, and therefore the blends of PHAs with other materials such as PLA, woody fibers, etc. as plastic composites are often employed.

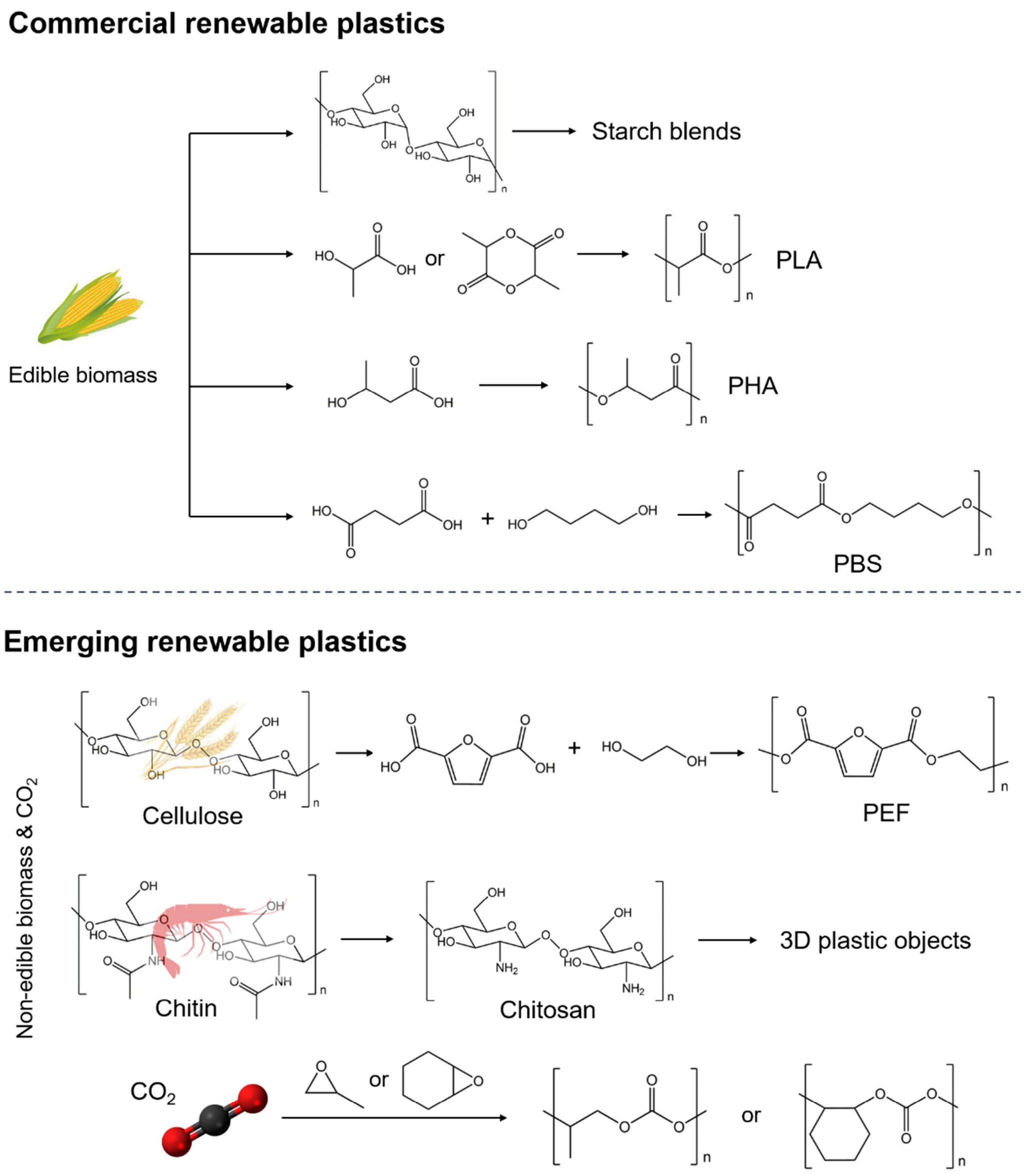

Figure 5 An overview of current commercial renewable plastics from edible biomass and emerging renewable plastics from non-edible biomass and CO_2.

4. Emerging renewable plastics

4.1 Renewable plastics from woody waste

Cellulose is the world's most abundant biomass with wide availability in agricultural and forest waste including wheat straws, corncobs, etc. 5-HMF has been ranked as one of the top value chemicals by the US Department of Energy, which is a versatile platform compound that can be derived from cellulose. The upgrading of 5-HMF can lead to the formation of 2,5-furandicarboxylic acid (FDCA), which is a building block to synthesize polyethylene furandicarboxylate (PEF). The biobased PEF plastic is a promising substitute to the fossil-based PET plastic which possesses a global market of about 15 million metric tons. Eerhart *et al.* have estimated that if all the PET products can be replaced by PEF plastics, around 440-520 PJ of non-renewable energy consumption could be saved with about 20-35 million tons of less carbon emission [25]. The catalytic oxidation of 5-HMF is a broadly studied strategy to obtain FDCA, and the relevant works were summarized by several excellent reviews [26-28]. The main bottleneck of the commercialization of FDCA-based plastic materials is still the high capital costs which should be reduced by future research endeavors such as process engineering, efficient catalyst development, etc.

4.2 Renewable plastics from ocean waste

So far most of the renewable plastics in the market are derived from edible biomass resources. New generations of renewable plastics from non-edible waste resources are highly desirable. Chitin and chitosan-based polymers receive increasing attention and emerges as one of the new renewable plastic materials. As the second most abundant biomass on earth, chitin is industrially extracted from waste crustacean shells (shrimp, crab, lobster shells, etc.), which is a linear polysaccharide consisting of

N-acetyl-D-glucosamine and D-glucosamine monomers linked by β-glycosidic bonds (see Figure 5). Although chitin boasts excellent biocompatibility and biodegradability, it has high crystallinity and insoluble in most of the common solvents, obstructing its widespread applications. Nonetheless, chitin nanowhiskers/nanofibers are synthesized as a natural, nontoxic filler to improve the mechanical property of renewable plastics such as starch [29].

Chitosan shares identical chemical backbone as chitin, and the only difference is the degree of deacetylation (DD%). After deacetylation treatment, chitin can be transformed into chitosan (DD% > 50%) which becomes soluble in acidic aqueous solutions. Due to the outstanding properties of easy-to-process, nontoxicity, antibacterial activity, biodegradability, biocompatibility, etc., chitosan has been utilized in a variety of fields such as food, biomedicine, agriculture, etc. [30-33]. Chitosan-based films are attractive in food packaging [34]. Not only eco-friendly, the antibacterial activity of chitosan benefits the food storage and prolongs the shelf life. The fabrication of chitosan-based films is relatively facile by direct casting, dipping, extrusion or layer-by-layer assembly, etc. In chitosan films, the liquid crystal domains (mm-scale) and the chain rearrangement when stretching were observed by analytical techniques such as birefringence microscopy [35]. In addition, three-dimensional (3D) plastic objects could be made by casting and injection molding (see Figure 6) [36], and various additives could be exploited to modify the properties of the chitosan plastics. By adding nanocellulose or other woody waste materials as the fillers, the chitosan/cellulose composites exhibited increased mechanical strength. By incorporating another type of ocean-based waste biomass, the alginate which can easily form composites with chitosan by electrostatic deposition due to the opposite charges, the thermal stability and the microstructures of the chitosan-based plastics can be adjusted. Besides, chitosan is inherently hydrophilic, by coating chitosan with a layer of hydrophobic materials such as Parylene, the chitosan-based plastic objects become water-resistant and thus can be used as cups and containers.

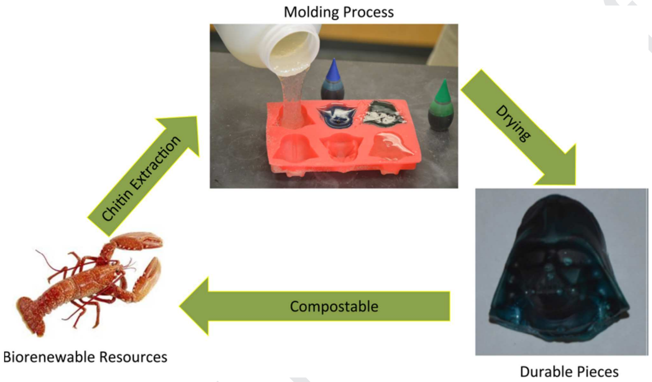

Figure 6 The scheme of fabricating chitin/chitosan-based 3D plastic objects. Reprinted with permission from Ref 36. Copyright 2015 American Chemical Society.

Albeit the prominent advantages, the viability of chitin/chitosan-based plastic materials are impeded by the problematic extraction protocol. Conventionally, the waste shells are first treated by concentrated, corrosive acids to remove the minerals and then strong bases to detach proteins, in which expensive equipment, careful handling and wastewater post-treatment are required. As a result, developing an economically and ecologically feasible approach for waste shell fractionation is a prerequisite to facilitate the practical uses of chitin/chitosan. Persistent efforts have been paid to explore new methods such as biological fermentation, solvent extraction, etc. [37-40], which boasts relative advantages but also obvious drawbacks such as the long process time, toughness for solvent recycling and low product purity. In 2019, a simple, economic, green and efficient protocol for waste shell fractionation was demonstrated, employing merely water and CO_2 as the chemical agents, which is patented as the HOW-CA process [41]. Furthermore, the protocol was proved scalable in the lab with detailed procedures displayed in Figure 7. Quantitative removal of proteins was realized at ~200 °C in water *via* partial hydrolysis and solubilization, since the subcritical water can generate protons and hydroxides that are able to promote acid- and base-catalyzed reactions. Afterwards, demineralization of calcium carbonate ($CaCO_3$) was conducted by the CO_2 pressure build-up and release cycle. The nature-mimicking process utilizes the weak acidity of CO_2 at high pressure to transform $CaCO_3$ into water soluble $Ca(HCO_3)_2$ which reprecipitates and separates from the chitin component upon pressure release. The overall purity of chitin product after HOW-CA process is beyond 90%. Besides, process modeling and life cycle assessment were exploited to show the economic and environmental superiority of the process to the traditional one. The progress in shell fractionation will expand the chitin/chitosan markets and foster their new applications such as the recent advent of "Shell Biorefinery" [42-49], which is to use chitin to produce a series of valuable nitrogen-containing chemicals.

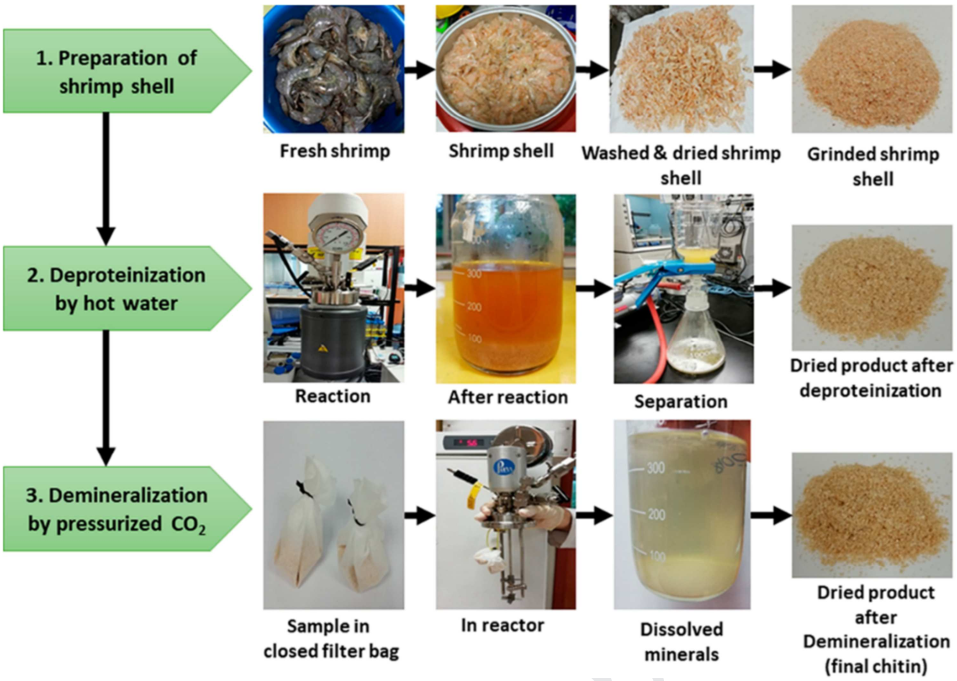

Figure 7 Images of processes involved in the HOW-CA process starting with 25 g of raw shrimp shells. Reprinted with permission from Ref 41. Copyright 2019 American Chemical Society.

4.3 Renewable plastics from CO_2

Utilizing CO_2 as a cheap, abundant and sustainable resource to produce valuable materials is distinctively propitious from both environmental and economic aspects [50]. CO_2 has been already used as a feedstock in chemical industries such as for the synthesis of urea. The conventional polycarbonates were generated by the condensation of bisphenol A and phosgene which is non-renewable and toxic. However, polycarbonate materials can be obtained by the copolymerization of epoxides and CO_2 which is partially sustainable and more environmentally friendly [51-53]. Future studies to produce the epoxides from biomass resources would make the process fully sustainable. Starting from epoxides and CO_2, the formation of cyclic carbonates is a competing reaction to the polycondensations. Homogeneous metal complexes were widely investigated as the efficient catalysts to facilitate the copolymerization especially Zn-based complexes. Ethylene oxide and propylene oxide are usually used as the monomer to co-polymerize with CO_2 to form aliphatic poly(ethylene carbonate) and poly(propylene carbonate). Nevertheless, the materials generally lack sufficient mechanical strength and low glass transition temperature which may obstacle the wide applications. Replacing the short epoxides with cyclohexene oxide will not only improve the polymer yield but also enhance the mechanical property and melting temperature. The poly(cyclohexene carbonate) has been regarded as a promising alternative to the traditional PS plastics.

Apart from utilizing it as a monomer constitute, CO_2 is also used as an indirect feedstock for renewable plastic production [54]. Methods such as electrosynthesis (ES), microbial electrosynthesis (MES), etc. is able to reduce CO_2 into various short-chain fatty acids including butyric acid, etc. Very recently, Sciarria *et al.* demonstrated the CO_2 reduction of the mixtures of acetate and butyrate in a bioelectrochemical reactor by the MES method [55], and utilize the formed short-chain fatty acid as the carbon sources to generate PHA plastics by biological fermentation. In the first step, 73% of the carbon was fixed into the organic acids by MES, and then purified as the feeding source for the biological fermentation. In the two-step scheme. The overall efficiency of carbon that transformed into PHA plastic was about 40%.

5. Challenges and outlook

There are still major hurdles to overcome in the future development of renewable plastics. The fossil-based plastic materials are advantageous over renewable plastics in terms of price. Advances in process design and engineering are anticipated to diminish the production costs, and as aforementioned next generation plastics should be formed from non-edible biomass waste. Besides, compared to the traditional plastics, the renewable plastic materials are less robust and less durable that cannot last for long-period use. They have restricted applications in sceneries where thermally stable, mechanically strong plastic materials are required. In addition, since renewable plastics exhibit different degrees of biodegradability, some of them are decomposed into organic compounds (instead of CO_2 and water) that enters the ecosystems which may cause unpredictable consequences.

To address these issues, scientists have innovated recyclable thermoset plastics with high mechanical strength and stability, and the polymer chains degrade and reconstruct in responses to environment variances (e.g. temperature, pH, etc.) [56-58]. In this way, the monomers are reusable for numerous cycles with minimal disposal, and thus the process becomes more sustainable despite the starting monomers are not derived from renewable resources. We also believe lignin as the world third most abundant biopolymer has potential to be a feedstock for renewable plastics [59-65]. The collaborative endeavors from academic researchers, chemical engineers, material scientists and relevant companies with their distinct expertise will advance the discoveries and establishments of excellent renewable plastics to shape a more green and sustainable society.

Conflict of interest

There are no conflicts to declare.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: