Alternative "green" lime kiln fuels: Part II—Woody biomass, bio-oils, gasification, and hydrogen

PETER W. HART

ABSTRACT: This paper is the second of a two-part series on "green" lime kiln fuels. The first part of this work reviews the use of pulp mill and recovery byproducts as either full or partial replacement of oil or natural gas in the kiln. The second part reviews the use of various forms of woody biomass, bio-oils, gasification and hydrogen as potential carbon neutral or carbon-free lime kiln fuels. Several of these options require specialized burners to supply the fuel to the kiln and high-quality metallurgy to withstand the acidic conditions of the fuel.

Application: Several "green" kiln fuels are identified to help reduce a mill's carbon footprint. Some, such as woody biomass, are readily available while others (e.g., various bio-oils) tend to be location specific. Some potential emerging options are also reviewed.

The lime kiln is usually the single largest user of fossil fuels in a typical kraft mill. As long as natural gas is relatively cheap, it will be the predominant kiln fuel in North America. Oil is the second most prevalent fuel, as an oil flame tends to increase the production throughput of the kiln by up to 10%. Both natural gas and oil contribute to the carbon footprint of the mill. There are several sources of "green" fuel that are available. The first part of this work focused on "green" fuel sources from byproducts from the pulping/recovery area. The current paper examines woody biomass sources, bio-oils, and gasification. The potential for using excess electricity to produce hydrogen as a kiln fuel is also reviewed.

WOODY BIOMASS

Woody biomass can be fed to the kiln in several diverse ways. It can be pulverized, dried, and blown into the kiln to undergo suspension burning. It can also be converted into a bio-char through light torrefaction, or it can be converted into a bio-coal through heavy torrefaction. These materials can also be turned into syngas, which can be used to heat the kiln. Gasification will be covered separately in a later section.

Pulverized wood and bark

Pulverized wood and bark are an obvious source of fuel for lime kilns. At least one mill, the National Swedish Forest Industries (ASSI) Lovholmen mill near Pitea, Sweden, has been firing wood residuals since 1980 [1]. To successfully fire wood and bark, it is important to sufficiently dry the material from about 40%–55% moisture in its natural state to 5% or lower. Drying the woody biomass will increase the heating value of the material and reduce the flue gas volume generated in the kiln from evaporation of the moisture.

The Lovholmen mill used boiler flue gas as the heat source for drying their biomass for the kiln. Some non-process element buildup problems in the liquor cycle were traced back to the flue gas from the power boiler, contaminating the drying biomass. During this time, the mill was burning peat in the power boiler. The flue gas contained aluminum, which was depositing onto the biomass and accumulating in the liquor cycle. The aluminum concentration got high enough that the mill was concerned about the potential to form aluminum silicate scale in the evaporators and modified their drying system to only use flue gas from the recovery boiler when drying biomass for kiln fuel. Several different heat sources can be used. Hot or warm water or recovered steam from the pulp mill will provide sufficient heat to dry the bark, as will flue gas. From a safety perspective, it is better to use steam or hot water, as the use of hot flue gas presents a substantial fire risk [2].

When processing wood and bark, it is important to remove extraneous sand and metals from the biomass to reduce wear on the equipment. It is also important to uniformly pulverize the material into a size that can be blown into the kiln and completely combusted so char specks do not appear in the lime [3]. The woody biomass fuel is typically pulverized to a size of 1–3 mm [4] for optimal firing in the kiln. A specially designed powder burner is required to successfully burn bark and woody biomass.

A series of tests was performed by PAPRICAN to determine if wood residuals could be burned for kiln fuel in a more natural state by in-situ combustion [3-6]. The idea

was to feed the woody material at 40%–50% moisture content into the cold end of the kiln along with the lime mud. The pretreatment requirements would not be as stringent or costly as those of firing wood residues in the burner, since the wood would not have to be ground as finely or dried as thoroughly. One of the drawbacks, however, is that once the biomass dries, most of it pyrolyzes in the 200°C–600°C temperature range, which means that a substantial portion of the volatiles pass unburned into the flue gases [7]. The additional moisture also adds to the total volume of flue gas potentially impacting fan-limited kiln production. In addition, any unburned char remains in the lime product. The work culminated in a mill trial where about 50% of the total fossil fuel was replaced by woody biomass. The mill trials were performed continuously for 44 days with no adverse impacts noted. It is unclear if this practice was every adopted at full scale.

The buildup of non-process elements in the relatively closed lime cycle is of great concern for operating kraft mills. It has been stated by Makie et al. that "unlike the cement industry, the pulp and paper industry cannot directly inject fuels, such as ground tires or bark, into the lime kiln because the ash and particulate carryover would cause contamination of the lime and pulp. This contamination would be extremely problematic given that the lime kiln is part of the closed-loop recovery cycle," [8]. Wood and especially hardwoods and bark, contain a significant quantity of trace elements and impurities. For instance, phosphorus (P) is present in wood chips at the start of the kraft process and accumulates in the lime cycle. Phosphorous does not react at any stage of the kraft recovery process until it enters causticizing. Once it gets to lime and caustic, phosphorous reacts to form calcium phosphate during causticizing.

Over time, calcium phosphate increases dead load in the lime cycle and must be removed [9]. A study by Abson and Holman looked at the effects of ash from wood residue firing in lime kilns on lime and liquor quality [10]. A direct outcome of the contamination of lime by fuel ash was found to be an influx of non-process elements (NPEs) into the liquor cycle. Bench-scale simulations of the causticizing cycle indicated that the main effect of ash contamination during calcination was the buildup of inert material in the lime cycle, resulting in increased dead load and increased fuel demand.

Observed impacts included a reduced settling efficiency of lime mud solids from white liquor in the causticizing area and a decrease in lime availability. The amount of inert material formed in the lime was considerably greater than the amount of ash added due to the sintering reaction between the ash and lime calcium oxide (CaO). The ash-derived inerts appeared to be mostly insoluble in white liquor, resulting in increased grits being removed from the lime cycle that resulted in increased makeup lime demand. The contamination of the liquor cycle by NPEs was mostly confined to the dissolution of about 40% of the ash aluminum, resulting in the potential for aluminum silicate scale formation in the evaporators [1]. In general, it is believed that some compromise would have to be made in terms of lime quality and/or lime makeup level if fuels like bark or hardwood are fired in the kiln on a full-time basis [11].

Torrefaction of woody biomass—Bio-char or bio-coal

The objective of torrefaction is to create a solid biofuel with high energy density and low hygroscopicity [12]. The process occurs between 220°C and 300°C in the absence of oxygen. Some researchers recommend limiting the reaction temperature to 280°C to retain reasonable energy efficiency [13]. Under the higher temperature conditions, the moisture is removed, and the hemicelluloses are degraded, causing the release of acetic acid, various phenols, and other compounds of low heating value [14]. Lignin also suffers a slight polymerization, resulting in a more brittle material that has intermediate characteristics between coal and biomass. For the optimum use in pelletizing, torrefaction, gasification, or pyrolysis processes, the moisture content of the raw material must be reduced to at most 10%–15%.

When wood or bark is torrefied, a significant amount of the total energy is lost. The process causes a reduction in the energy content of the biomass because of partial devolatilization that results in a significant loss of mass. The large reduction in mass results in an increase in the energy density of the biomass. The average is a loss of 10% to 17% energy for 30% to 38% of original mass, which results in a much higher density material that is easier to store and transport [15].

Different reaction conditions—such as temperature, inert gas ratio, reaction time, and wood type—may be used to produce different solid, liquid, and gaseous products. As temperature and time increase, for example, the solid yield decreases and the heating value (kJ/kg) of the resulting char increases. Another feature of torrefaction is that it reduces the hydroscopic property of biomass. As a consequence, torrefied wood products are relatively hydrophobic and absorb less moisture when stored as compared to wood or bark. The higher energy density makes torrefied biomass very attractive for combustion and gasification applications.

Torrefaction units have been designed with energy efficiency in mind. In most of the unit designs, torrefaction gases are combusted in an afterburner [16], and the flue gas is used to provide the majority of the heat necessary for the drying and torrefaction processes. In cases where the internal off gases are not sufficient, the use of flue gas from a lime kiln or medium pressure steam may be used as a supplemental, low oxygen content heat source.

Torrefaction significantly reduces the oxygen and hydrogen content of biomass while increasing the carbon, nitrogen, sulfur, and ash content of the resulting torrefied material. Table I shows the ultimate analysis of wood and bark and of the resulting torrefied products obtained from them.

	C	H	O	N	S	Ash	HHV
	Ultimate Analysis, wt% on dry basis						MJ/kg
Wood	48.00	6.50	45.20	0.10	trace	0.20	19.72
Lightly torrefied wood	59.84	5.44	33.41	0.22	0.01	1.08	23.80
Highly torrefied wood	71.30	3.40	19.33	0.23	0.34	5.40	26.80
Bark	52.00	5.51	36.21	0.56	0.04	5.68	20.76
Torrefied bark	53.30	3.46	14.36	4.03	0.31	24.54	20.64
C = carbon; H = hydrogen; O = oxygen; N = nitrogen; S = sulfur; HHV = higher heating value.							

I. Ultimate analysis showing the impact of torrefication on wood and bark [17].

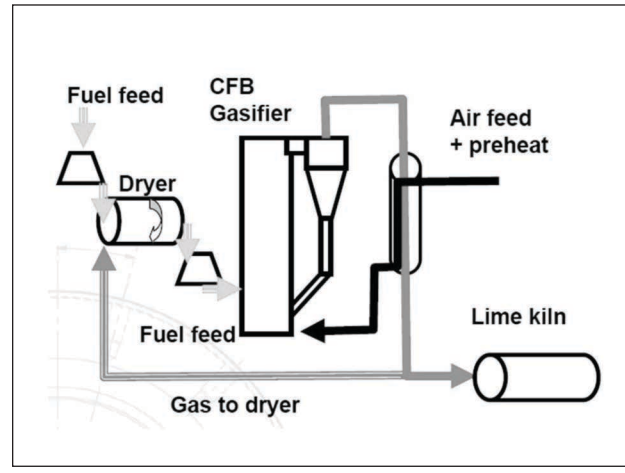
Torrefication of wood can be performed either lightly (low level of mass loss), resulting in a bio-char, or highly, resulting in a bio-coal. One important note from **Table I** is the substantial increase in ash resulting from torrefication. The ash levels will result in a buildup of NPEs, causing increased grits, increased lime makeup demand, increased fuel demand, and poor settling in the clarifier.

GASIFICATION

To reduce the buildup of inert and non-process element materials in the lime cycle, some mills have started gasifying their organic materials and operating the kiln on syngas (a.k.a., producer gas) [18-20]. This technology is not new. Fixed bed wood residual gasifiers were employed in Sweden during World War II. South Africa has used coal gasification and several European mills employed gasification of wood and bark during the 1980s; at least two of these mills still employ the technology [58]. More recently, equipment vendors have been supplying circulating fluidized bed (CFB) gasification technology to produce syngas integrated with a lime kiln. **Figure 1** shows a schematic of a typical integrated CFB/lime kiln unit [19-21].

Even when using gasification technology, some attention needs to be paid to the buildup of NPEs in the kiln. Some ash and dust will end up in the kiln, and critical elements such as silicon (Si), aluminum (Al), iron (Fe), magnesium (Mg), potassium (K), and phosphorus (P) need to be monitored. For instance, in the Värö mill, lime bleed is used specifically for control of the P in the lime system [19, 21].

Another set of major concerns with syngas from wood residues has been its low heating value compared to natural gas or fuel oil. Depending on the gasifier operating conditions, wood residue type, moisture content, and whether oxygen or air is used, the higher heating value of syngas may vary widely, from 3.5 to 11.5 MJ/kg (1500 to 5000 Btu/lb), as compared with 53.2 MJ/kg (22300 Btu/lb) for natural gas and 43.1 MJ/kg (18400 Btu/lb) for fuel oil. In some syngases, small particulate matter will enter the kiln with the gaseous vapors. These particles will glow when they get hot enough and increase the heat flux to the lime bed,



1. Schematic of an integrated circulating fluidized bed (CFB) gasifier and lime kiln [21].

thus slightly enhancing the heating value of the fuel. The low heating value means that more fuel is required to achieve the same heating rate, leading to greater amounts of exit gases going to the flue gas handling system and the possibility of exceeding the system capacity. In addition, a higher gas flow rate through the kiln can also lead to increased gas velocities, which may cause more dusting to occur and put an additional strain on the flue gas handling system. Other challenges include lower flame temperatures, temperature profiles that differ from those of natural gas and fuel oil, and introduction of NPEs into the kiln, particularly when the cyclones are ineffective, allowing ash and particulates to enter the kiln along with the syngas [22].

Historically, there have been three common types of gasifiers used in supplying syngas to lime kilns. These are updraft, downdraft, and fluidized bed devices [23]. Other types of gasifiers do exist. **Table II** shows the difference in fuel and air flow, as well as the biomass bed support mechanism and heat sources, for the three different types of gasifiers [24].

The simplest gasifier is the updraft type. It consists of a fixed biomass bed lying on a grate, up through which heat-

Gasifier Type	Flow Direction		Support	Heat Source
	Fuel	Air		
Downflow fixed bed	Down	Down	Grate	Partial combustion of volatiles
Upflow fixed bed	Down	Up	Grate	Combustion of char
Circulating fluidized bed	Up	Up	None	Partial combustion of volatiles and char

II. Classification of different gasifier types [24].

ed air is blown. Combustion occurs at the lowest levels of the fixed bed, supplying gasified material and heat to the upper levels of the bed. As the oxygen-depleted combustion gases rise through the bed, they cool off and force slow pyrolysis of the biomass in the upper levels of the bed. A significant quantity of oils and tars are generated through the slow pyrolysis process. Careful temperature control is required at this point in the process and is difficult to obtain. If the temperature is too low, the tars and oils will condense out of the syngas. If the temperature is too high, the tars and oils will undergo cracking reactions. The resulting gases may contain 10% to 20% of the original biomass as tar residue.

Other than temperature control, a typical problem is that ash melting can occur in the exit gas ductwork, causing the system to plug. If the biomass particle size is allowed to vary and to have lots of quite fine material, the fixed bed tends to condense upon itself and prevent gas throughput or it forces the gases to channel through the bed. Most updraft gasification units are connected to power boilers. Several operate with a good quality, uniform size wood chips to prevent bed collapse and facilitate temperature control. The few units connected to lime kilns are typically operated with coal instead of wood or bark [25].

A downflow gasifier has far less tar related issues. Air is injected between the pyrolysis zone and the combustion zone. Heat from the biomass (traditionally coal) drives pyrolysis in the upper part of the reaction vessel. Tar and oils drop down through the combustion zone and crack into hydrogen and carbon monoxide, which exit in the flue gas. Heat transfer from the combustion zone to the pyrolysis zone tends to be the operational bottleneck for these types of units. Hence, these units are always relatively small scale. Also, a large portion of the material in the combustion zone tends to remain unburned, resulting in a high overall fuel demand or low producer gas conversion rate [26].

The most common gasification unit integrated with lime kilns today is the fluidized bed system [19]. The first one was started up in 1983 at the W Schauman mill in Pietarsaari, Finland. This unit ran virtually trouble free for many years [23]. The fluidized bed unit (shown in Fig. 1) consists of a vertical refractory-lined tube with an air distribution grid at the bottom. Air is blown from the bottom through the grid into a loose packed sand bed consisting of 0.2 to 2.0 mm particles. Air velocity is increased until the sand takes on the appearance of a bubbling liquid. When the sand has been heated to 850°C–950°C, biomass is introduced into the boiling bed of sand. Because the amount of oxygen in the reactor is substantially sub-stoichiometric, some of the biomass is combusted, providing heat for the pyrolysis reactions while the remaining material undergoes pyrolysis and forms syngas. Most of the ash is entrained in the combustion gases and separated in a cyclone at the exit of the unit.

A measurable portion of carbon char is also entrained in the combustion gas and also removed from the syngas in the cyclone. To improve reaction efficiency, modern fluidized bed units introduce finely ground biomass into the lower middle of the reaction vessel where there is virtually no oxygen present so it can dry, volatilize, and be lifted towards the top of the reactor. A large portion of sand and unburned char are then recycled from the top of the reaction vessel back to the bottom of the vessel above the air distribution grid, through a refractory lined downcomer, and then reburned. The char and ash are separated in the cyclone and dropped back into the reaction vessel below the air distribution grid where the char can burn in an oxygen rich atmosphere and provide heat for the pyrolysis above. Ash is removed from the area under the grid by gravity though a valve at the bottom of a conical section. Typical production rates account for 98% to 99% of the organic portion of the biomass entering the unit being successfully converted into syngas. Ash removal has been demonstrated to be approximately 93% successful. The separated ash was found to contain less than 1% carbon.

Research efforts have evaluated the potential to gasify a considerable number of organic sources to replace fossil fuels in the lime kiln. Mill derived sources include wood and wood residuals such as bark, knots, and screen rejects; precipitated lignin; and sulfate soap recovered from black liquor [25]. Other sources of biomass potentially include urban forest residuals, such as construction waste and products diverted from landfills; fast-growing energy crops (e.g., short rotation hardwoods) [27]; agricultural residuals [28,29] like corn cobs, corn stover, and straw; and herbaceous energy crops like switchgrass and miscanthus [24]. Of all of these options, wood is the most commonly used biomass fuel for gasification integration with a lime kiln, with coal (a fossil fuel) being a close second [25]. The most economic sources of wood for fuel are usually wood resi-

	Ultimate Analysis, wt% on dry basis						Proximate Analysis, wt% on dry basis			
	C	H	N	O	S	Ash	Moisture*	Volatiles	Fixed Carbon	HHV, MJ/kg
Agricultural Residues										
Sawdust	50	6.3	0.8	43	0.03	0.03	7.8	74	25.5	19.3
Bagasse	48	6.0	--	42	--	4	1	80	15	17
Corn cob	49	5.4	0.4	44.6	--	1	5.8	76.5	15	17
Short Rotation Woody Crops										
Beech wood	50.4	7.2	0.3	41	0	1.0	19	85	14	18.4
Herbaceous Energy Crops										
Switchgrass	43	5.6	0.5	46	0.1	4.5	8.4	73	13.5	15.4
Straw	43.5	4.2	0.6	40.3	0.2	10.1	7.6	68.8	13.5	17
Miscanthus	49	4.6	0.4	46	0.1	1.9	7.9	79	11.5	12
Municipal Solid Waste										
Dry sewage	20.5	3.2	2.3	17.5	0.6	56	4.7	41.6	2.3	8
Coals										
Subbituminous	67.8	4.7	0.9	17.2	0.6	8.7	31.0	43.6	47.7	24.6
Bituminous	61.5	4.2	1.2	6.0	5.1	21.9	8.7	36.1	42.0	27.0

C = carbon; H = hydrogen; O = oxygen; N = nitrogen; S = sulfur; HHV = higher heating value.
*Biomass moisture contents reported are for dried feedstocks.

III. Ultimate and proximate analysis of potential biomass gasifier feedstocks [24].

dues from mills, discarded wood products diverted from landfills, and non-hazardous wood debris from construction and demolition activities. Specially grown trees like eucalyptus show promise for the future, since they have the potential to be genetically tailored to grow fast, be drought resistant, and be easily harvested. The ultimate analysis and proximate analysis of several potential feedstocks were determined for an NREL study and are shown in **Table III**.

In general, each mill has a specific reason for choosing to use gasification as a replacement for fossil fuels. For most mills, the reason is economics [30]. For instance Pertti Lehmonen, the project manager for the gasifier installation at the Metsä Fibre Joutseno pulp mill in Lappeenranta, Finland, has stated:

> The availability of low cost biomass at this mill was a key driver for us choosing gasification technology. We have a woodyard, but no bark boiler at the Joutseno mill, so we have plenty of wood residuals available [19].

Other mills simply want to enhance their carbon footprint and enhance their "green operation" [30]. Some mills would like to use other sources of fuel for gasification, but substantial research and development questions must still be answered. For instance, the most important open questions around using black liquor soap are related to good atomization of soap and the sodium capacity of lime kilns [31].

BIO-OILS

According to the 2008 Global Survey on lime kilns conducted by TAPPI, at least 6 kilns are currently firing bio-oils [30]. There are a number of mills that did not respond to the survey but are known to have used alternative fuels. Bio-oils come from multiple sources. Several are processed from various vegetable and animal sources, while others are created through wood/biomass pyrolysis reactions. One bio-oil is actually a byproduct of biodiesel manufacturing.

Bio-oils are often counted as carbon neutral "green" fuels, and they are usually free from carbon dioxide (CO_2) or energy taxes. When considering a bio-oil as a lime kiln fuel, potential sustainability and ethical aspects should be considered. Use of food crop-based, first generation (1G) bio-oils for energy production can have wide social impacts

and increase food shortages in poor countries. Widespread clearing of vegetation to make room for bioenergy plantations can result in indirect CO_2 emissions if large carbon stocks such as dense rainforests are harvested. Use and harvesting of wood-based bio-oils can decrease habitat diversity and destroy landscapes [9].

Vegetable oils

Vegetable oils can be extracted from a variety of different crops growing all over the world. Usually, oils are extracted from soya or oil palm, but nowadays there are also more unusual variants in the form of almond oil, hazelnut oil, rapeseed oil, and cottonseed oil. Fresh fruit branches of palm trees are collected and taken to crude palm oil mills where the fruits are crushed to produce crude palm oil. Crude palm oil is then usually taken to a refinery where it is fractionated into a lighter liquid fraction called palm oil olein and a more viscous fraction called palm oil stearin [32]. The more viscous fraction is often mixed with other oils to enhance flow characteristics.

Animal fat

Another source of bio-oil is liquefied animal fat. At least one pulp mill in Brazil is currently burning filtered and liquefied animal fat in their lime kiln. Animal fat comes from a nearby meat processing plant, and the fuel used in the kiln is oil derived from the fat called olein. Olein is made up of fatty acids, but ultimately it consists mostly of carbon, hydrogen, and oxygen. It has a higher heating value that is almost the same as heavy fuel oil [9,22,30].

Glycerin—a biodiesel byproduct

Some mills have fired glycerin or glycerol as a partial replacement for natural gas. Glycerol is a major byproduct in the biodiesel manufacturing process. In general, for every 100 lb of biodiesel produced, approximately 10 lb of crude glycerol are created and must be disposed of by the producer. When biodiesel manufacturing was rapidly expanding during the late 2000s, a glut of glycerin was produced [33]. Some mills basically purchased crude glycerin for shipping costs and bled a small amount into their recovery boilers as a supplemental fuel [34].

Crude glycerin is not an acceptable fuel for use in a lime kiln. The relatively high moisture content renders the net heating value too low and increases the amount of flue gas produced by the kiln. Additionally, the firing of glycerin must be closely monitored to ensure complete combustion. Incomplete combustion of glycerin in a kiln can result in measurable emissions of acrolein, a volatile organic substance that smells like burning fat and causes burning of the nose and throat. It can damage the lungs [35].

Crude glycerin has been partially dehydrated using multiple techniques, such as centrifugation. Some of these methods have successfully reduced the water content to 5% or less, which produces an acceptable lime kiln fuel. Some kilns have operated at 25% BTU substitution for natural gas for several weeks using this upgraded glycerin. About the time glycerin processing methods were successfully implemented for upgrading the material to kiln standards, an alternate use as animal feedstocks was discovered, making the use of upgraded glycerin cost prohibitive.

Pyrolysis oils

The pyrolysis of wood residues is an interesting alternative for pulp mills. The resulting bio-oil can replace fossil fuels in the lime kiln [36]. One advantage for pulp mills would be the potential to store pyrolysis oil and burn it when needed. However, the phase-separation and polymerization of the liquid bio-oil, as well as the high corrosion rates of storage vessels containing pyrolysis oils, make storage of these liquids challenging [36]. Therefore, it is recommended to continuously consume the oil as it is produced. Most mills would rather gasify their woody biomass to produce a syngas for kiln fuel than deal with the high moisture content, corrosive tendencies, and acidic nature of pyrolysis oils. The limited storage life due to polymerization is also a major concern for mills. Considerably more research will be required before pyrolysis oils become a major alternative kiln fuel.

HYDROGEN

Modern, well-designed pulp mills (non-integrated) are net energy producers. In fact, in a modern pulp mill, the only consumer of fossil fuel could be the lime kiln. Frequently, biomass and black liquor are burned to produce high pressure steam that is used to produce electricity. The mill is operated with extraction steam taken from the turbines. As such, some of these mills have a large excess of electrical power. Studies have been done to determine the feasibility of using some of this excess power to produce hydrogen via electrolysis to be used as a lime kiln fuel source [37].

Alkaline electrolysis is a known, commercial technology [38] that can quite easily be integrated into a pulp mill process. The process consists of an electrolytic cell that separates water into hydrogen and oxygen while producing heat. Cooling water is required when the reaction cell is operating and may be used as a low-grade source of heat elsewhere in the mill. The oxygen that is generated could potentially be used in the bleach plant or in an oxygen delignification stage to offset self-generated or purchased oxygen already in use at the mill. Storage of hydrogen is relatively difficult and as such, the highest value potential consists of using an electrolytic cell that is integrated with the lime kiln.

Burning hydrogen in a lime kiln typically requires a modified valve train and injection system. It does not create problems when it is co-fired with other fuels. Hydrogen is co-combusted, for instance, at the Stora Enso Oulu mill in Finland and at the UPM Fray Bentos mill in Uruguay [28,39]. Burning hydrogen can be challenging due to ex-

tremely high flame temperatures and flame propagation velocities. It is essential to maintain high exit velocities at the burner tip in order to stabilize combustion at the tip and not overheat the burner [40]. Hydrogen systems use specially designed valve trains and special lances for burning in the kiln.

Hydrogen handling and storage issues are a result of its very low density and its ability to leak through extremely small openings. If an electrolytic cell is used in an online, integrated manner, there is no need for hydrogen storage, which makes the process both simpler and safer. Water quality requirements vary a little depending on the type of electrolytic cell employed, but it can be assumed that existing water treatment equipment at the mill can be used to purify water for this process. This increases the load at the water treatment plant.

In addition to specific purpose hydrogen generation, mills with on-site production of sodium chlorate ($NaClO_3$) generate hydrogen as a byproduct of the chlorate reaction. For mills that are located near a $NaClO_3$ plant, or for larger bleached pulp mills equipped with their own $NaClO_3$ plants, hydrogen is available and is often one of the fuels burned in the lime kilns.

In a theoretical case study for a large Brazilian mill, it was determined that the mill produced enough electricity to power an electrolysis system large enough to supply about 73% of the lime kiln fuel demand [37]. Cooling of the electrolytic cell was estimated to produce 34% of the mill's hot water demand. The load on the water treatment plant was calculated to increase by 12%. The study determined that the hydrogen-via-electrolysis scenario offers a promising new alternative for utilization of excess electricity produced in a modern pulp mill. It is typically only economical when electricity prices are low or selling of electricity is not possible due to local conditions.

Some research efforts have looked at alternative approaches to producing hydrogen for kiln fuel. Various methods examined include the catalytic reforming of bio-oil to produce hydrogen, the use of bio-oil as a feedstock in gasification, and a Fischer-Tropsch process to produce hydrogen and diesel fuel. Although these methods are interesting alternatives, they are not economically viable with current technology [41].

SUMMARY

Woody biomass in various forms has been successfully used as an alternative "green" fuel for lime kilns. When using these materials in the kiln, buildup of NPEs is a concern and often results in the need to purge more grits and lime mud from the system. Several different bio-oils have also been successfully used in kilns. When using these materials, the food-versus-industrial use conundrum must be determined before a mill switches to these fuels. Pyrolysis oils have potential, but more work is required before they will be widely accepted as a kiln fuel. Producer gas, obtained from woody biomass application, has also been successfully used in kilns, but the heating value is rather low, making it difficult to control. Several of these materials require special burners. Many are corrosive and require special metallurgy in the storage tanks and supply piping. If the price of natural gas and fuel oil escalate or if a mill is interested in substantially altering its carbon footprint, there are several different options available, depending upon cost and local supply conditions. **TJ**

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ABOUT THE AUTHORS

The current work is part of a new book on lime kilns and recausticizing from TAPPI Press. This area is less represented in the available literature and in need of its own text. The current work looks at alternative "green" fuels that can be used in the kiln. It summarizes the multitude of available options and discusses their pros and cons.

The most difficult aspect of this work was identifying the plethora of fuels available for use in the kiln. All of these green fuels are highly cost dependent, and the corrosivity of several of these available alternative fuels was somewhat surprising. It would be nice to use green fuels, but the cost structure will make them extremely location dependent and somewhat unlikely, unless the cost of oil and gas escalates or government programs impact the cost structure.

For mills, the current work identifies multiple fuel options and outlines potential issues with their use. The next step would be to monitor the various options and compare them with the cost of fossil fuels, working to determine what works best for each mill location.



Hart

Hart is director, Fiber Science and Innovation, for WestRock, Richmond, VA, USA. Email Hart at peter.hart@westrock.com.

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