CHAPTER 14

THE ENERGY SECTOR: A HIDDEN GOLIATH

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1. INTRODUCTION

Energy from wood is the most significant single use for the world’s wood harvest. During the last decade more than 50% of the annual 3-3.5 billion m³ wood production was used directly as fuel. The rest of the wood harvest provides feedstock for sawmills, pulp mills and wood-based panel manufacture. Each of these processes creates significant residues suitable for energy production, typically 20-40% of the total wood feedstock. Thus, if the wood processing industry’s supply of a significant proportion of its own energy needs from residues is taken into account currently 60-70% of all wood harvested is used as fuel.

Energy from biomass (including wood) currently represents approximately 14% of the world’s primary energy supply, about 40 EJ/yr – 1 EJ or 1 ExaJoule or 10¹⁸ J represents approximately the energy consumption of a small, developed country with a population of about 5 million people. 40 EJ/yr represents only 40% of what is easily possible: a conservative estimate of the total sustainable world biomass energy potential is about 100 EJ/yr or 30% of our current total energy consumption. Wood’s share of this is estimated as 41.6 EJ/yr (Parrikka, 2004). However, projections suggest that almost 400 EJ/yr of energy could be available from biomass in 2050 (50% of the world’s projected energy demand). The increase in demand for biomass (including wood) as energy depends on the availability and cost of fossil fuels. Currently oil, natural gas and coal provide cheaper, more convenient but more environmentally damaging sources of energy. The developed countries rely heavily on fossil fuels for energy, with only 2% of total energy consumption being derived from wood, although it varies from country to country. In Sweden and Finland (Ericsson et al., 2004), encouraged by supportive government policy and a readily available wood supply, forest biomass contributes almost 20% of primary energy (Figure 14.1). In contrast in developing countries much of the domestic and industrial energy supply comes from wood and charcoal. Indeed in 13 developing countries, wood provides 90% or more of their total primary energy consumption and in a further 21 countries more than 70% (Trossero, 2002). In total the developing countries consume about 75% of the world’s woodfuels. Unfortunately in the majority of developing countries woodfuel use is via inefficient technologies
Figure 14.1. Energy supply in terawatt hours (1 TWh = 10^12 kWh) in Sweden for 1970-2003.

Figure 14.2. Major end uses for wood and bark in the United States, in M m^3 or M tonnes, data from Koning and Skog (1987), Waddell et al. (1989), Ulrich (1988) and USDA (1990).

that utilize only about 10-15% of the energy available from the supplied wood, with the majority of the energy supplied as heat alone. In contrast, the developed countries use wood wastes far more efficiently to deliver a variety of energy types
(electricity, heat and liquid fuels) but this is a tiny proportion of total consumption. Figure 14.2 shows the wood flows for energy and wood products through the United States wood industry.

The challenge for energy production from wood is twofold. First to increase its share of energy supply in the developed countries; and secondly to retain and to grow its share of energy supply in the developing countries while introducing modern bioenergy production technologies. The versatility of wood as an energy source when coupled with the appropriate conversion process is shown in Figure 14.3. Choosing the appropriate pathway can deliver energy as electricity, heat, alcohols, synthetic gasoline and diesel, methane or hydrogen. In short, all of the energy products are possible that citizens of developed countries take for granted but that come largely from fossil fuels. Unfortunately, the lack of impact of this most sustainable of energy sources is poignantly summarized by noting that world fuelwood use was estimated at 1.7 billion m$^3$ in 1800, about the same as direct fuelwood use today (Schulz, 1993). However, with increasing urgency the world

![Figure 14.3. Alternative energy pathways using wood.](image-url)
recognizes that climate change is inevitably associated with fossil fuel use and it is this realization that may finally awaken the sleeping giant of woody biomass energy.

2. CHARACTERISTICS OF WOOD AS A FUEL

One attractive and distinctive feature of wood is that it is a readily renewable resource. It has a very low ash content and is free of sulphur and other obviously polluting or corrosive elements. In almost all other respects the characteristics of wood are less desirable than alternative fuels:

- Wood is approximately 50% carbon, 44% oxygen and 6% hydrogen by weight. Since wood is highly oxygenated it is understandable that it has only about two-thirds of the calorific value of coal, which is pure carbon. The calorific value of oven-dry wood is about 20 MJ kg\(^{-1}\). This varies slightly between species, with resin rich woods having higher calorific values and non-resinous species having lower calorific values. Its ash content is less than 1%, which is very low compared to coal.
- The volatile fraction of wood is about 80% whereas with coal it is only 20-30%. The volatile fraction burns first leaving the residual carbon (charcoal). The volatiles contribute to air pollution if they are not completely burnt. Clean burning of volatiles is the key to efficient wood-burning.
- Wood contains moisture, and energy must be spent unproductively in evaporating this moisture (Table 14.1). Also, the evaporating moisture forms a boundary layer on the surface of the wood, which makes ignition more difficult. More significantly, when burning wet wood the furnace temperature is depressed and at low temperatures combustion is often incomplete so further reducing thermal efficiency. While it is desirable to reduce the moisture content of the wood or chips this is not always practical or economic and some processes have to be adapted to cope with this situation. Variations in moisture content require good process control if combustion is to be efficient.

<table>
<thead>
<tr>
<th>Moisture content, oven-dry basis (%)</th>
<th>Net energy available (MJ kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18.2</td>
</tr>
<tr>
<td>15</td>
<td>15.4</td>
</tr>
<tr>
<td>30</td>
<td>13.5</td>
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<tr>
<td>45</td>
<td>11.9</td>
</tr>
<tr>
<td>60</td>
<td>10.5</td>
</tr>
<tr>
<td>100</td>
<td>8.0</td>
</tr>
<tr>
<td>200</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*Table 14.1.* The net calorific value of wood depends on its moisture content: here the values are for a typical hardwood. The reduction in available energy with moisture content is due to the need to vapourize and superheat the steam to the same temperature as the flue gases. Typically the net calorific value for a hardwood is 18.2 MJ kg\(^{-1}\), that for a softwood is 19.2 MJ kg\(^{-1}\) (due to its higher lignin content) and that for bark is 19.7 MJ kg\(^{-1}\) (due to extractives).
- Wood is not a premium fuel. It is bulky to transport, difficult to handle unless chipped, and is of moderate calorific value. Its energy per unit volume is low: obviously denser timbers contain more woody material and therefore have a higher energy content per unit volume. Traditionally it is used for raising process steam and heating, mainly by the forest industries, and in domestic stoves.

Bark is often combined with wood residues and burnt. Bark has a fractionally higher calorific value and can be used equally in boilers and for the production of methanol following gasification. However bark can only be used in ethanol production if gasified first rather than via the conventional process based on the conversion of the polysaccharide components of wood.

When wood is heated an enormous variety of chemicals are produced: water vapour, non-condensable gases (carbon monoxide, carbon dioxide, hydrogen and methane), pyrolysis products (methanol, acetone, acetic acid, and complex hydrocarbons and volatile tars). A carbon-rich char (charcoal) remains. The relative proportions of these products vary depending on the amount of oxygen admitted, on the temperature and on the physical configuration of the furnace.

Initially heat is needed to drive off the sorbed water and raise the temperature of the wood to about 275°C. Once this temperature is reached the wood constituents begin to break down spontaneously (pyrolysis). Sufficient heat evolves for the decomposition and the release of volatile products to be self-sustaining, and the temperature rises further. Oxygen is not necessary. At even higher temperatures the tars and oxygenated hydrocarbons crack to simpler gases. These gases can be mixed with oxygen in the air supply and burnt. Combustion involves the decomposition of wood, the burning of volatile gases (degasification) and the production of a carbon-rich residue (charcoal). The furnace temperature rises further (400-600°C) which accelerates the decomposition of the wood. Eventually the volatile fractions are all driven off and the flame diminishes. The wood charcoal comes in contact with the in-coming air and becomes incandescent.

Air is passed through the fuel chamber to ensure as complete combustion as possible. In practice excess air is needed because of imperfect mixing of gases and because the additional volume of air helps prevent condensation of residual unburnt pyrolysis gases and water vapour in the flue. Condensation in the flue is more likely when the wood is wet and when the fire is starved of air. By increasing the draft the temperature at which condensation occurs in the flue is lowered, which is beneficial. However excess air means that the heating efficiency is diminished as more heat escapes up the chimney. Thermal efficiencies for cooking, hot water and spaceheating can be as high as 80% with a well designed, enclosed stove compared to 20% with an open grate or three-stone fire (Gilmour and Walker, 1995).

3. CHARCOAL

FAO (1983) estimates that some 400 Mm³ of roundwood a year, about a quarter of all fuelwood, is first converted to charcoal before being used. In cities in developing economies charcoal is a preferred cooking fuel because it is smokeless, light and so
cheaper to transport, more energy intensive than wood, and burns with a much hotter flame. In monetary terms charcoal, per unit mass, is approximately ten times more valuable than wood.

Wood for charcoal production must first be cut, split and dried because wet wood has a low heat value. In the moist tropics it is difficult to hold timber in stack for more than a couple of months without noticeable deterioration, but even in that time the moisture content can drop from 60% towards 30%. Stock holding also ensures continuity of supply.

In a traditional charcoal kiln some of the wood is burnt in order to completely dry the rest of the wood, and to raise the kiln temperature until pyrolysis reactions release sufficient heat for the process to become self sustaining (>300°C). The air vents are then sealed and the volatile gases and tars together with non-condensable gases such as carbon monoxide, carbon dioxide, hydrogen and methane are driven off. Only a proportion of these volatiles is burnt. These chemical by-products are not recovered and much of the potential heat available from pyrolysis is wasted. The temperature stabilizes around 400-450°C. When most of the volatile fraction has been driven off the chimney is also sealed and the kiln allowed to cool. The warm-up time is typically a day or so, pyrolysis takes 20-30 days to convert most of the wood to charcoal, followed by a cool-down period of equal duration before the charge is unloaded. With simple technologies the recovery of charcoal is low, about 15-20% by weight on an oven-dry basis, with at best 6 m³ of roundwood yielding a tonne of charcoal. The charcoal has approximately 50% of the energy of the wood, while having only 20% of its original weight. With better designed kilns conversion efficiencies of 30-35% are achievable. The quality of charcoal from a traditional kiln is quite variable. It depends on the wood, its moisture content and the rate of burn. Poorly prepared charcoal can retain as much as 50% by weight of volatile material. This has the advantage of igniting easily but it burns with a smoky flame. Charcoal picks up moisture quite rapidly and when sold this can range from 5-15%, increasing with the increasing impurity of the charcoal.

An efficient kiln requires good insulation (thick walls of brick or earth) and must be well sealed so as to exclude air when desired. During the warm up-period air is drawn into the kiln through openings in the wall and these are only sealed once the colour of the smoke in the chimney changes from white to thin blue, indicating that the charge has been dried and there is no more moisture to be driven off. When pyrolysis is complete the smoke hole is sealed as well to exclude all air and the kiln left to cool. In simple kilns it is extremely hard to ensure even heating throughout the kiln. Typically part of the charcoal will be burnt while some wood elsewhere in the kiln will only be lightly charred.

Sophisticated and capital intensive kilns seek to recover the heat from the combustible gases and use this to preheat the in-coming wood, rather than relying on the partial combustion of the wood itself. Such continuous kilns operate at higher temperatures and the resultant charcoal has a much smaller volatile fraction in the charcoal, making it more suitable for many commercial purposes where purity is important, e.g. in smelting metals. This high quality charcoal is pyrolysed at higher temperatures (450-550°C) and has about 30% by weight of volatile material. Modern kilns use a variety of cheap plant residues including sawdust and bark and the
residence time in the kiln is only a few hours. The fines are briquetted with the help of a starch binder.

4. FAST PYROLYSIS OF WOOD

Traditional pyrolysis of wood relies on low temperatures and long processing time to increase the charcoal yield. In contrast, modern or fast pyrolysis uses moderate temperatures (400-500°C) and very short residence times (typically only a few seconds) to maximize the production of liquids (Diebold and Bridgewater, 1997). Pyrolysis vapours are rapidly cooled and condensed after leaving the reactor to prevent cracking into smaller molecules. The main product is a ‘bio-oil’ obtained in yields of up to 75% by weight of the dry wood feed. Char and non-condensable gases are also produced at yields of between 10-15% of the wood feed. The bio-oil and char are commercial products while the non-condensable gases are recycled to the reactor and burnt to provide the endothermic reaction heat. Bio-oil is a dark brown, free flowing liquid mixture of several hundred different chemicals. An approximate composition is 20-25% water, 25-30% water-insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars and 10-25% other oxygenated compounds. It has a calorific value of 16-19 MJ/kg and is a potential substitute for fuel oil and natural gas used in boilers, gas turbines and diesel engines. Bio-oil has about 40% of the energy content of fuel oil on a mass basis and 60% on a volumetric basis because of its comparatively high density (1.2 kg/litre). The fast pyrolysis reactor has required much research but it represents only about 15% of the capital cost of the process. Feedstock for fast pyrolysis requires considerable preparation to guarantee successful processing. It must be dried to less then 10% moisture content to limit the water content of the product and ground to a small size (approximately 2 mm) to encourage rapid reaction. This adds to the final process equipment cost. Large scale bio-oil production via fast pyrolysis is nearing commercialization (Thamburaj et al., 2000).

5. WOOD GASIFICATION

Wood gasification is a key stage in the production of useful energy (heat and electricity) and fuels from wood. Wood gasifies to make a ‘producer gas’, a mixture of hydrogen, carbon monoxide, carbon dioxide, methane and hydrocarbon/tar components. The gas has a heating value of anywhere from 3-20 MJ/Nm³, depending on whether the gasification occurs using either air or a steam/oxygen mixture. Producer gas was used as long ago as the mid 19th century to fuel gas lights in London and, later, in the early 20th century automobiles. The carbon oxides and hydrogen can be recombined to make alcohols and liquid hydrocarbons, a far more convenient way of fuelling today’s vehicles.

Gasification occurs by heating wood to a high temperature (1200-1400°C) in an oxygen deficient atmosphere, so limiting combustion. The process has four phases; drying, devolatilization, gasification and combustion. Wood fuels vary in moisture content from about 10-50% water so the first phase is heating and drying the wood.
In the second phase, of devolutilization or pyrolysis, light gases including hydrogen, carbon monoxide, carbon dioxide, water, methane, higher hydrocarbons, and tar (heavy organic and inorganic molecules) are driven off leaving a reactive char. The char gasifies by reacting with oxygen, CO$_2$ and water to produce more carbon oxides and hydrogen. In the gas phase, the water gas ‘shift reaction’ alters the relative amounts of carbon monoxide and water compared to carbon dioxide and hydrogen, while the tar and heavier hydrocarbons react with oxygen to produce lighter gases. The key to gasification success is in the controlled partial combustion to yield a gas with a high heating value.

5.1. Gasification reactions

The generalized gasification reaction can be written:

$$[\text{CH}_{1.44}\text{O}_{0.66}] + \text{H}_2\text{O} + \text{O}_2 = \text{H}_2 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 (+ \text{tar/hydrocarbons}) \quad (1)$$

wood

The ratios of hydrogen or oxygen to carbon are almost constant in all woods and it can therefore be represented by a single molecular formula. Where air is used rather than oxygen the produced gas mixture will contain nitrogen and be less valuable. This equation is a deceptively simple summary of many reactions. The more important ones occurring, after devolutilization, can be broken into two groups. The first are char gasifying reactions;

$$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO} \quad (2)$$

$$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO} \quad (3)$$

$$\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 \quad (4)$$

The second group are gas phase reactions. The hydrocarbons formed during devolutilization break down to form hydrogen and carbon monoxide:

$$\text{C}_x\text{H}_{2y} + x\text{H}_2\text{O} \rightleftharpoons x\text{CO} + (x+y)\text{H}_2 \quad (5)$$

Tar cracking reactions to produce simpler gases also occur, as long as the residence time in the reactor is sufficient. Gaseous components can rearrange via the water gas shift or methane formation reactions;

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (6)$$

$$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad (7)$$

The overall result is a fuel gas mixture of carbon oxides, hydrogen, methane, water and any remaining tar and heavier hydrocarbons that escape the gasifier. Some of
the reactions are exothermic and some endothermic but the overall gasification process is endothermic and requires an external energy source.

5.2. Gasifier designs

There are three variants of gasifier design: updraft, downdraft and fluidbed. The oldest form of gasifier is the updraft variation. Wood particles (chips or pellets) are fed in the top of the gasifier while gasifying agents (air or oxygen plus steam) are fed in the bottom. The wood feed dries, pyrolyses, gasifies and combusts as it moves downwards, the solids exchanging heat and reacting with the gas phase. Ash is withdrawn from the bottom and the produced gas, along with entrained wood particles and tar, leaves from the top.

In the downdraft version both the wood and gasifying agents move downwards through the gasifier, and produced gas and ash leave from the bottom. The same four stages occur but the gas produced during devolatilization must pass through the high temperature combustion section. This promotes tar breakdown and produces a cleaner gas than the updraft version. Further, when compared to the updraft version, controllability limits the operational size to smaller diameters of reaction vessel in the downdraft version.

In the previous two gasifier versions the wood moves slowly through the vessel due to gravitational forces. Individual wood particles remain in contact with their neighbours. In a fluidised bed, gas is injected into the bed of wood particles at a high enough flowrate that individual particles detach and move randomly within the fluid bed volume. If gas rate is increased further a bubbling fluid bed results. Here, the wood particles continue their separate movement but bubbles of gas form rising through the bed without mixing with the solids. The solids can still be identified as mainly residing within a defined volume above the grate although there will be some small carryover of finer particles leaving with the gas stream. If the gas velocity is increased further ultimately the gas and solids flow as a single stream through the gasifier. The solids are then said to be entrained by the gas flow and the fluidised bed region is no longer identifiable. Gasifiers can operate in both the bubbling and entrained flow regimes. The main advantage of a fluidbed gasifier is that reaction conditions can be more closely controlled and similar gasification performance and gas production expected over a significant size range.

A high calorific value fuel gas mixture is produced if oxygen and steam are used. With air (20% O₂, 80% N₂) a large amount of nitrogen is included in the produced gas, inevitably reducing its calorific value. However, high purity oxygen is expensive and its extra cost makes gasification financially less attractive. Steam alone can be used but without oxygen the exothermic combustion reactions that supply energy are missing. To reduce the air supply a variant on gasification design combining an entrained and bubbling fluidised bed was developed. A fast internally circulating fluidised bed (FICFB) gasifier combusts char, from gasification, in a bed of sand fluidised in the entrained flow regime with air. The heated sand is carried out the top of the first fluid bed and sent to the gasification section, which is fed with wood chips or pellets, and the combined wood/sand bed fluidised with
steam. The hot sand supplies energy and normal gasification occurs, producing a gas mixture uncontaminated with nitrogen. Figure 14.4 shows the FICFB concept (Hofbauer et al., 1997).

![Diagram of FICFB concept](image)

*Figure 14.4. Fast, internally circulating fluidised bed gasifier.*

5.3. Combined heat and power systems

Medium scale wood gasifiers (10-30 MW thermal capacity) have attracted significant interest and development investment in recent years because they can be integrated with industrial processes to supply heat and electrical power, i.e., combined heat and power (CHP) or cogeneration systems. The large size of the energy flows effectively limits these applications to fluidised bed gasifiers. The most efficient system initially burns the produced gas in a gas turbine to generate electricity. The hot exhaust gases are used in a waste heat recovery boiler to produce a lower pressure steam to run a steam turbine, generating further electricity. Any residual low grade heat in the gases from the heat recovery boiler can be used around the process plant (for example, to dry wood if the process is a sawmill) or in a district heating scheme. The total combined heat and power process is known as a biomass integrated gasification and combined cycle (BIGCC) system and is shown in Figure 14.5.

Gas turbines are sensitive to corrosion and erosion from wood particles and tar compounds that can escape from the gasifier so a necessary extra process step is gas cleaning to produce turbine quality fuel gas. Conventional cogeneration schemes consist of biomass combustion, steam generation and then electricity generation using a steam turbine. The advantages of the BIGCC system are a higher electricity generation efficiency (up to 48% vs. conventional 29%) and higher proportion of
electricity to thermal energy production (0.9-1.1:1 vs. 0.29:1 for conventional systems). Its disadvantages are extra complexity and capital cost when compared to conventional cogeneration systems.

A limited number of large scale BIGCC systems have been built and operated around the world in the last 10 years. Well known examples are the ABRE scheme in the UK (8 MW electricity generation or MWe, using atmospheric biomass gasification), the Varnamo scheme in Sweden (6 MWe and 9 MW thermal or MWh capacity, using pressurized gasification) and the FICFB system at Gussing in Austria (2 MWe and 4.5 MWth, where the produced gas is burnt in a gas engine rather than fed to a combined cycle system). These demonstration projects have all been technically successful but have struggled to compete economically, mainly because of their high capital cost. However, the BIGCC technology is technically feasible and further development will see it become more successful financially.

![Image](Figure 14.5. Biomass integrated gasification and combined cycle system.)

**6. WOOD AS A FEEDSTOCK FOR LIQUID FUELS**

Wood is a mixture of carbon, hydrogen and oxygen atoms that can be rearranged into liquid fuels using appropriate processing steps just like oil, natural gas or coal. Principal liquid fuel products from wood are methanol, ethanol or Fischer-Tropsch liquids (this is a complex mixture of hydrocarbons). The alcohols can replace gasoline while Fischer-Tropsch liquids replace diesel, providing renewable rather than fossil fuels for conventional combustion engines. There are two well-developed methods for manufacturing fuels from wood. Gasification, using oxygen or a FICFB gasifier, is the key processing step in the first of these two approaches. The producer gas from gasification can be manipulated by altering the ratio of carbon oxides to
hydrogen to become synthesis gas, which becomes the feedstock for producing all three liquid fuel products. Methanol and Fischer-Tropsch liquids are made via a chemical route by passing the synthesis gases over appropriate catalysts at high pressures and temperatures, while ethanol is produced biologically by fermenting the gas.

The second method is direct fermentation of wood sugars, recovered from the polysaccharides, cellulose and the hemicelluloses, by acid hydrolysis to produce ethanol. This is a proven technology whereas synthesis gas fermentation is as yet successful at only a small scale. The main advantage of synthesis gas fermentation is that all the wood components, including lignin, become a potential source of ethanol. In direct fermentation lignin must be separated out from the feed to the fermentor.

The energy efficiency of these processes (Energy in the product/Energy in the feed) is summarised in Table 14.2.

Table 14.2. Energy efficiency of wood fuel production (GJ/GJ).

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Methanol</th>
<th>Ethanol (SG)</th>
<th>Ethanol (F)</th>
<th>F-T liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>0.29-0.65</td>
<td>0.35*</td>
<td>0.3</td>
<td>0.16-0.43</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0.61</td>
<td></td>
<td></td>
<td>0.54-0.63</td>
</tr>
<tr>
<td>Corn</td>
<td></td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>

* There is more uncertainty associated with ethanol production from syngas. SG = Synthesis Gas, F = Fermentation (Spath and Dayton, 2003).

Comparative figures for methanol and F-T liquids from natural gas are included. The higher conversion efficiencies and lower processing cost explain why natural gas is the feedstock of choice rather than wood. This is understandable because natural gas is largely methane with a low C:H ratio. Ethanol is commonly produced by direct fermentation of corn sugars in the USA at a similar efficiency to producing the alcohol from synthesis gas. However, wood is a renewable feedstock.

A second energy balance description, emphasising renewability, is the fossil energy ratio defined as the energy in the product divided by the total fossil fuel derived energy consumed from feedstock procurement through product generation. The fossil energy ratios using wood are wood-to-methanol = 12-26, wood-to-ethanol (SG) = 16 and wood-to-F-T liquids = 6-17. Fossil energy ratios for natural gas systems are all less than 1 because the main source of energy consumption is the feedstock itself and it cannot be converted into another energy source without expenditure of energy. Life cycle analyses studying corn ethanol production suggest a fossil energy ratio of only 1.3 because of the large input of fossil fuels required for farming corn, including significant amounts of fertilizer (natural gas sourced). Clearly ethanol from wood is considerably more renewable than corn ethanol.

Wood as a source of liquid fuels is still largely untapped because of the still easy availability of cheap natural gas and the comparatively more developed and consequently efficient processing routes. The looming spectre of world climate
change will accelerate adoption of wood for fuel systems in the first half of the 21st century.

7. METHANOL PRODUCTION

Synthesis gas from wood for methanol production is produced by gasifying with a mixture of steam and oxygen. The oxygen can come from either cryogenic separation of oxygen from nitrogen in liquefied air or by the electrolysis of water. The most efficient commercial gasifiers are fluidised beds that use a restricted supply of pure oxygen and operate at temperatures and pressures at or in excess of 900°C and 5 MPa. The aim is to maximise gas production with no ancillary charcoal. An alternative gasification scheme would be to use a FICFB gasifier that would produce synthesis gas of similar composition to pressurised oxygen gasification. Wood has a molar ratio of hydrogen to carbon of 1.44:1 while the corresponding ratio in methanol is 4:1. Inevitably, synthesis gas from wood contains excess carbon if used for methanol production. The proportion of hydrogen to carbon monoxide in the synthesis gas can be adjusted using the water gas shift reaction. The excess carbon monoxide is reacted exothermically with water over an iron-chrome catalyst to generate hydrogen and carbon dioxide.

\[ CO + H_2O = CO_2 + H_2 (> 2 \text{ MPa, } 850^\circ\text{C}) \] (8)

This process helps to correctly balance the gas mixture but now there will be too much carbon dioxide which must be stripped out using absorbing amine or hot bicarbonate solution.

However, if electrolysis of water were used to provide oxygen for the gasifier the hydrogen produced at the same time would correct the hydrogen/carbon monoxide ratio.

Methanol is synthesized from the carbon oxides and hydrogen using a copper based catalyst at 200-300°C and 5-10 MPa. The reaction is exothermic and the released heat can be used to generate high pressure steam:

\[ CO + 2H_2 = CH_3OH \] (9)

also

\[ CO_2 + 3H_2 = CH_3OH + H_2O \] (10)

Since the reaction reaches equilibrium with only a partial conversion (5%) of the reactants to methanol a system to recycle the synthesis gas is used. After cooling to condense out the methanol and water the remaining gases are recycled to the reactor in what is basically a closed loop.

A recent process development may lead to simplified plants for methanol manufacture from synthesis gas with a high carbon oxides to hydrogen ratio. Commercial methanol catalysts in fine powder form are suspended in inert mineral
oil and the synthesis gas bubbled through the catalyst slurry. Heat removal by producing steam is more efficient than in a gas phase reactor and the reaction temperature is more uniform allowing higher conversion and a lower recycle rate. The water gas shift and carbon dioxide removal steps are also no longer required as synthesis gas rich in carbon oxides can be fed straight to the reactor. The crude methanol (methanol/water and small amounts of impurities) is refined by distillation to produce fuel grade methanol. The net usable energy of the methanol represents around 30-60% of the total energy inputs to the gasification and methanol plant (Table 14.2).

Currently methanol is used largely as a feedstock for the manufacture of formaldehyde and a range of chemicals. It has considerable potential as a liquid fuel either directly or via a fuel chemical derived from methanol. For example, methyl tertiary butyl alcohol (MTBE), produced by reacting methanol with isobutene, has been a popular blending agent for gasoline because it improves octane rating. In the future, biodiesel, produced by reacting methanol with naturally occurring oils and fats, is likely to become a substitute for fossil fuel sourced diesel.

8. ETHANOL PRODUCTION FROM SYNTHESIS GAS

Ethanol is the only renewable liquid fuel made in commercial quantities and supplies about 1% of the gasoline type transport fuels used in the USA. Approximately 95% of the commercial production of ethanol in the USA is currently by direct fermentation of corn-sourced carbohydrates. However, fermentation of synthesis gas has the advantage over direct fermentation of sugars from cellulose and the hemicelluloses in that all wood components, including lignin and bark, are suitable feedstocks.

The first step in the process is gasification of wood followed by conditioning and cleaning of the synthesis gas to give a mixture rich in CO and H₂. The synthesis gas is sparged into a broth-filled tank fermentor where bacteria (Clostridium ljungdahlii, for example) convert CO and CO₂ to ethanol via the following two reactions:

\[
6\text{CO} + 3\text{H}_2\text{O} = \text{CH}_3\text{CH}_2\text{OH} + 4\text{CO}_2 \tag{11}
\]

\[
2\text{CO}_2 + 6\text{H}_2 = \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \tag{12}
\]

The resulting fermentation broth is quite dilute, 2% ethanol or less. The ethanol can be recovered from the broth using distillation schemes developed for the existing corn to ethanol manufacturing process (Spath and Dayton, 2003).

9. FISCHER-TROPSCH LIQUIDS

Ethanol and methanol are useful gasoline substitutes. However, a diesel replacement can also be produced from wood using Fischer-Tropsch synthesis (Spath and Dayton, 2003). The first step is once again high temperature gasification using oxygen and steam to make synthesis gas, followed by cleaning of the gas to prevent damage to the catalyst and adjustment of the gas composition using the water gas
shift reaction and carbon dioxide removal (Eq. 8). The required ratio of hydrogen to carbon monoxide for Fischer-Tropsch synthesis is approximately 2:1. A ‘chain growth’ reaction occurs over an iron or cobalt catalyst involving sequential addition of -CH₂- groups to produce an alkyl chain of increasing length:

\[ \text{nCO} + 2\text{nH}_2 = \text{C}_n\text{H}_{2n+2} + \text{nH}_2\text{O} \]  

(13)

The reactor operates either at low (200-240°C) or high (300-350°C) temperatures and between 1-4 MPa. The product mix changes from longer to shorter chain length molecules as the temperature increases. The product stream from a Fischer-Tropsch reactor is a mix of many components but by selecting the right operating conditions the mix can be adjusted so that the product stream has mostly diesel fuel properties.

10. HYDROLYSIS OF WOOD

Any treatment of wood must take account of the differing accessibilities and reactivities of the principal wood constituents. Further, any chemical or microbial method of breaking down wood has to devise conversion pathways for cellulose, the hemicelluloses and lignin, and if necessary consider ways of isolating the individual reaction products so that they can be processed separately. Hydrolysis has proved to be a most effective method of opening up the wood structure for subsequent treatments. The expression ‘hydrolysis of wood’ is used rather loosely. It is not technically correct since the reactions affect primarily the carbohydrate fraction of wood. Lignin is largely unaffected.

Although composed predominantly of polysaccharides wood has little value as an animal feed except as supplementary, non-nutritional roughage (Hajny, 1981). The complex lignin-carbohydrate structure of wood, the crystallinity of the cellulose, and the inaccessibility of the cell wall to large enzyme molecules makes wood resistant to the action of cellulytic microorganisms. Softwoods are non-digestible while hardwoods are at best slightly digestible. *Populus tremuloides* is an exception having significant digestibility (40%). Presteaming hardwood chips dramatically enhances their digestibility by cellulase enzymes in a ruminant's stomach. Presteaming involves heating the wood chips in a pressure vessel at temperatures between 230 and 150°C for a period of time ranging from a few seconds to an hour or so. The mass is then explosively discharged by 'blowing' the digestor. The chips are well disintegrated. The presteaming of hardwoods is often described as autohydrolysis as the acids which catalyse hydrolysis are generated by the process itself, rather than being added as a separate ingredient as in acid hydrolysis. Presteaming of the hemicelluloses yields acetic, formic and other acids which lower the pH further so enhancing the depolymerization of the hemicelluloses and to a lesser degree the lignin, but leaving the cellulose largely unaffected. During presteaming the hardwood hemicelluloses hydrolyse readily to water-soluble, low molecular weight fragments (oligomers), the relatively abundant acetyl and carbonyl groups are cleaved, and the α-ether linkages in lignin are hydrolysed. The cleavage of many cross linkages makes the cell wall of hardwoods much more accessible to
cellulase enzymes. Under optimal conditions presteaming of hardwoods is an effective pretreatment prior to a microbial or chemical route for the manufacture a variety of chemicals from the polysaccharides and lignin.

Softwoods need slightly severer conditions than those provided by steaming (Clark and Mackie, 1987). Hydrolysis proceeds much faster with the addition of sulphur dioxide which is an effective acid catalyst (Figure 14.6). The enzymatic digestibility of the cellulose in the insoluble residue increases with progressively severer cooking conditions (higher temperatures, longer cooking times and more sulphur dioxide). For example, when treating softwood chips at 215°C for 180 s their digestibility increases from around 5% to over 80% with the addition of 2.5% SO₂. The cellulose is attacked and about 25% of this is solubilized, pyrolysed or degraded. Further glucose (5%) comes from the glucomannans. The improved enzymatic digestibility appears to be related to the complete removal of hemicelluloses and a partial removal of some cellulose which allow the cell wall capillaries to enlarge. The cellulase enzymes are no longer physically excluded

Figure 14.6. Hydrolysis of Pinus radiata chips (Clark et al., 1989). Enzymatic digestibility and the overall carbohydrate survival are improved by the addition of SO₂ during presteaming. The water-insoluble fibre yield after washing decreases with increasing SO₂, while its digestibility (defined as the yield of glucose after 72 hr, expressed as a percentage of the theoretical yield) increases with increasing amounts of SO₂. It is clear that most benefits from using SO₂ are achieved with a SO₂ level of about 2-3%.
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from the cell wall because of their size. Further, structural and chemical changes such as fibre fragmentation (frequently separating the $S_2$ from the rest of the cell wall) and partial depolymerization, repolymerization and coalescence of lignin into droplets within the cell wall at these high temperatures (Donaldson et al., 1988) all favour subsequent enzymatic hydrolysis of the cellulosic residues. However, compared to the autohydrolysis of hardwoods, softwood lignin after acid hydrolysis is much less soluble in NaOH, presumably because of repolymerization of lignin fragments which is favoured by highly acidic conditions.

When the treated chips are blown from the digester they disintegrate into a mass of fibre and fibre fragments. Washing the exploded pulp extracts the soluble components which includes dimers and higher molecular weight fragments (oligomers). Sugar monomers are recovered after further mild hydrolysis. The solids, predominantly cellulose and lignin, can be hydrolysed under harsher conditions or treated with enzymes to extract sugars. The total sugar yield is related to polysaccharide solubilization and survival (of the water-soluble fraction), and to the enzymatic digestibility of the steam exploded fibre (the water-insoluble fraction). At near optimal conditions (180 s at 215°C with 2.5% SO$_2$) the total sugar yield is 57 g/100 g of oven-dry wood, consisting of 29 g of sugars from the water-soluble extract and 28 g after enzymatic digestion of the solids (Clark et al., 1989). Of this approximately 40.6 g is glucose, a further 11.4 g are other hexose sugars and the balance, 5.4 g, are pentose sugars.

11. ETHANOL PRODUCTION BY ACID HYDROLYSIS AND FERMENTATION

Acid hydrolysis, with dilute sulphuric acid hydrolysis in particular, has been the traditional way of breaking down wood to recover fermentable sugars (Figure 14.7). The cellulose in the microfibrils is not readily accessible and moderately harsh conditions are necessary to make the process viable. A practical limitation in the hydrolytic decomposition of the polysaccharides to sugars is that the sugars themselves are subject to simultaneous degradation to chemicals such as furfural, so the sugars can never be recovered in full: yields can be as low as 50% of the theoretical value. The former Soviet Union developed a major commercial wood hydrolysis programme with some 40 such units. Much of this was fermented to single cell protein for cattle feed. Production was around 800 000 tonnes a year of yeast fodder (Wayman and Parekh, 1990). It is unlikely that the process would have been economic in a free market economy.

Although hardwoods have a lower lignin content and so give a higher yield of sugars, softwoods are preferred where ethanol is the desired end product. This is because hardwoods have more pentose sugars, which are not readily fermented by common yeasts. In a typical batch process sawdust and wood chips are loaded into the reactor vessel and treated with dilute sulphuric acid (0.5% concentration) at temperatures between 130 and 200°C for about three hours. Ideally, the sugars should be removed from the reaction zone before they, in turn, have time to break down.
Figure 14-7. Ethanol production from wood (Burton et al., 1984).

A two-stage operation is more efficient (Uprichard and Burton, 1982). Initially the temperature is 130-140°C and the dilute acid attacks the hemicelluloses, which hydrolyse very much faster than cellulose, and their sugars and other decomposition products are drawn off prior to the main acid hydrolysis stage. At this point, about 30 minutes, the temperature is raised to 180-190°C under pressure (1.6 MPa) and cellulose hydrolysis begins. Acid is introduced continuously at the top of the vessel and the dilute sugars are drawn off continuously at the base. Acid, so necessary for hydrolysis, must be neutralised and removed prior to fermentation. Slaked lime, Ca(OH)₂, is added to neutralise the acid and to prevent further degradation of the sugars. The solution is filtered and flash cooled. The byproduct gypsum, CaSO₄, finds uses in the manufacture of wall panels and in fertilisers. The 130-140°C pretreatment not only allows recovery of the sugars from the hemicelluloses, also it increases the subsequent rate of hydrolysis of cellulose and allows the glucose to be drawn off more quickly so that simultaneous degradation of the sugars in the reaction zone is reduced. With pine the yield of sugars is about 64% of the theoretical yield. Once the carbohydrate material has been broken down into its constituent sugars the undissolved lignin in the hydrolysis tank is flushed out. It can be used for process energy or possibly as a chemical feedstock in its own right.

New developments aim to increase the yield further, by relying on fast (< 1 min), high temperature (> 240°C) and continuous hydrolysis. At higher temperatures the rate of hydrolysis of cellulose increases more rapidly than does the rate of degradation of the newly formed sugars so it should be possible to obtain a slightly better yield.
The hexose sugars, glucose and mannose, are subsequently converted to ethanol by fermentation with a yeast such as *Saccharomyces cerevisiae* within the first 12 hours at 35°C:

\[ C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2 \]  

This fermentation process is the same as that used for ethanol production from cane sugar except the sugar concentration is lower, so distillation costs are greater. The ethanol is recovered and concentrated by distillation. Ethanol yields of 20% of the oven-dry weight of wood are obtainable. Purity is not a major concern as many byproducts (esters, higher alcohols etc.) are also good fuels. Galactose, the only other abundant hexose sugar, is virtually unused after 24 hours and does not contribute to the ethanol yield. It remains unconverted in the stillage. The yeast-rich stillage, containing the pentose sugars and other hydrolysis products, can be converted to methane using anaerobic bacteria. Anaerobic digestion removes much of the organic matter in the waste water system while generating a very substantial quantity of methane. The production of methane (CNG) substantially enhances the overall efficiency and process economics, while greatly relieving a major effluent problem. The overall thermal efficiency is about 50% with half arising from ethanol production (24%) and half from the surplus methane (27%) which is in excess of that needed to provide process heat (Burton et al., 1984).

The process described by Burton et al. (1984) uses proven technology and demonstrates the point that the production of ethanol from wood is likely to be viable only when integrated as a multiproduct operation. The obvious areas for improvement are in increasing the ethanol yield and in encouraging fermentation to continue as the concentration of ethanol builds up in the solution, which would significantly reduce the cost of distillation.

### 12. ETHANOL VIA SIMULTANEOUS SACCHARIFICATION AND FERMENTATION

An alternative to the well established but relatively inefficient acid hydolysis of wood is enzymatic hydolysis using the cellulase enzyme. Research at the National Renewable Energy Laboratory in the USA since the late 1980s has focused on a generation of genetically engineered cellulase enzyme systems. These are combined with yeasts to allow simultaneous saccharification (liberation of sugars from cellulose) and fermentation of those sugars to ethanol: sugars are continuously produced by the enzymes and converted by the yeasts to ethanol. Organisms capable of fermenting these sugars from cellulose and the hemicelluloses are now available, increasing the theoretical yield of ethanol in comparison to acid hydolysis processes. A recovery of about 380 litres of ethanol per tonne of wood is achievable, equivalent to 80% of the theoretical yield (Wayman and Parekh, 1990). The first step in the process is a dilute acid treatment (0.5% sulphuric acid) at high temperature (190°C). This splits up the hemicelluloses into their constituent sugars and renders the cellulose more accessible for enzymatic breakdown. The liquid hydolysate contains...
acetic acid and other inhibitors in addition to the hemicellulose sugars. The treated hydrolisate is combined with the residual solids (cellulose and lignin) from the hydrolysis step and sent to the simultaneous saccharification and cofermentation (SSCF) tanks. The fermentors are dosed with a combined cellulase/yeast inoculum – an example fermentation microbe is Zymomonas mobilis which is capable of fermenting both glucose and xylose. The cellulase is produced in additional fermentors using an industrial fungus, Trichoderma reesei for example, that feeds on a small, diverted amount of the main fermenter feedstock. A dilute ethanol stream (approximately 2% ethanol) is then concentrated by distillation followed by molecular sieve dehydration to produce fuel grade ethanol. Waste water containing lignin and other organics is anaerobically digested to produce biogas and the residual lignin solids are burnt as fuel. SSCF is already almost cost competitive with acid hydolysis processes and it is expected that the discovery of more efficient microorganisms will make SSCF the more attractive process in the next 5-10 years. The main improvement is the anticipated development of ethanol producing microorganisms capable of working at higher ethanol concentrations (5%) and at higher temperatures (50°C). Increased ethanol concentration reduces the cost of ethanol concentration and increased temperature dramatically increases saccharification rate, reducing the cost of the required cellulose enzyme. Potentially the production cost per unit of alcohol could be halved, making lignocellulosic ethanol competitive with gasoline at current prices.

13. LIQUID FUELS

The fermentation of sugar cane to produce ethanol has been adopted by Brazil in its effort to develop a local fuel for domestic transport. Pure petrol/gasoline is no longer available and cars in that country run on either a 22-25% blend of ethanol with petrol or on pure ethanol. In 1987 ethanol consumption in transport was equivalent to 7.5 million metric tonnes of oil (Trindade and Carvalho, 1989) and it continues to be used at about that level. Brazil has the available land for sugar cane production and made the decision to develop alternative liquid fuels in 1975 despite the fact that the cost of production was very substantially greater than the cost of the equivalent oil imports. If oil prices are greater than around $US$40/barrel there is an economic incentive to expand Brazilian ethanol use. However, if the oil price drops to $US30/barrel then ethanol is only just cost effective. Oil prices were less than this during the 1990s and this stalled growth in ethanol use. In 2005, because of high oil prices the Brazilian ethanol program looks set for expansion. In the United States corn-based ethanol is more expensive than compressed natural gas (CNG) and methanol but survives because of generous subsidies resulting from continued lobbying by agricultural interests and because it can be blended with petrol and used in vehicles without engine modification. Brazil and the United States account for more than 95% of all ethanol production from biomass.

Few countries apart from Brazil have developed alternative fuels to displace petrol in transport. In Europe biodiesel, a replacement for fossil diesel manufactured by reacting methanol with fats extracted from oilseeds, is starting to make an impact
but consumption is still small. Elsewhere alternative fuels have made at most a limited contribution to a nation's overall liquid fuels strategy. Their use is likely to remain peripheral unless severe dislocations in energy supplies or rapidly rising fossil fuel prices make their production viable. However concerns about the uncertainty of supply and regarding previously ignored social costs due to air pollution and global warming need to be taken into account in policy. The cost to society of air pollution can only be guessed. Estimates for the United States range from only ten billion dollars to almost two hundred billion dollars annually (Sperling, 1989) without taking into account the economic impact of global warming. A major shift to alternative fuels is beginning in areas such as southern California, basically in response to appalling air quality.

Both compressed natural gas (CNG) and methanol are much less polluting than petrol. Neither is competitive with petrol on a narrow economic analysis. Of the two, methanol is probably viewed more favourably. It may appear illogical to convert natural gas into methanol rather than using it as CNG, but the ability to transform a gas (or solid if wood were to be the feedstock) to a liquid fuel outweighs the cost and energy required to effect that conversion. However, part of the support for methanol is pure inertia, emphasising the difficulties in setting up an extensive distribution system for CNG, the cost of vehicle conversion, the need for bulky fuel tanks, and the limited fuel range. Motor vehicles are designed to use liquid fuels and are burdened with redundant fuel systems when retrofitted to use compressed natural gas. By contrast modifications for methanol fuelled vehicles are much simpler.

The other major alternative fuel is ethanol. Ethanol is more polluting, although less so than petrol, but it has the advantage in that it can be blended with petrol or used by itself (with minor modifications to the engine).

The potential for manufacturing liquid fuels from wood will remain unfulfilled until the technology and economics move in its favour or the negative impact of poor air quality and global warming are considered significant enough to overturn conventional economic decision making. Few countries have the land available to dedicate to a woody fuels programme. Wayman and Parekh (1990) calculate that it would require 10% of the total land area of the United States to meet its requirements for liquid fuel – about 100 million ha of dedicated forest plantations.

14. ENERGY AND CLIMATE CHANGE

Between 1850 and 1998 atmospheric carbon dioxide levels have risen from 285 to 366 ppm, mainly because of the combustion of fossil fuels and changes in land use from forestry to agriculture. This unbalanced release of stored carbon is now generally accepted as setting us on a global climate change trajectory with an unknown but likely to be unpleasant destination. Combustion of fossil fuels alone contributed 6.3 Gt (gigatones or $10^7$ tonnes) of carbon dioxide emissions annually between 1989 and 1998.

Trees have a key role to play in slowing climate change. Their growth and integration into the energy system can help in three ways:
• If wood replaces fossil fuels as an energy source it directly and permanently reduces greenhouse gas emissions. Wood energy is carbon emission friendly as trees, planted to provide fuel, grow absorbing the carbon dioxide released by transformation of wood from previous harvests (combustion, gasification or conversion into liquid fuels followed by combustion) into energy. Wood energy is almost carbon emission neutral as long as only small amounts of fossil fuel are used to grow, harvest and transport the wood fuel source.

• Even if not used for fuel forests can act as sinks, storing carbon as long as the forests are never cleared and the land subsequently used for a different purpose. The problem, especially in the period that human population has increased rapidly, is a steady trend of deforestation to create agricultural land. It is impossible to guarantee that this will never happen to any of the world’s forests so offsetting emissions is not as permanent a solution to climate change as replacing fossil fuel with woody biomass.

• Using wooden building materials can cut out emissions associated with the production of the replaced more energy-intensive materials such as concrete, steel and aluminium.

Integration of wood directly into the energy supply system is the most permanent solution. Studies have shown that CO₂ emissions per kWh in a wood-fired power station are only 5-10% of the equivalent emissions from coal fired electricity generation. Ethanol from wood could potentially reduce greenhouse gas emissions by 65% on a per-mile travelled basis in comparison to gasoline if the replacement fuel is an 85% ethanol blend with petrol. If global biomass energy supply reaches 100-400 EJ yr⁻¹ by 2050 then this would potentially reduce greenhouse gas emissions by between 20-55%.

Global climate change represents one of the strongest drivers for making wood to energy schemes a reality. However there will be only a slow uptake of the possible technologies as fossil fuel based systems are inevitably cheaper because conventional economics does not account for their adverse environmental effects. The Kyoto protocol is the first attempt to encourage bioenergy use by setting a target of 5% less than their 1990 greenhouse gas emissions for developed countries to meet in the first commitment period of 2008-2012. Signatories to the protocol have to find ways of meeting their targets using instruments such as carbon credits to encourage carbon friendly schemes and carbon taxes to discourage fossil fuel users. These measures slightly weight the economics of energy schemes in favour of bioenergy over fossil fuels but they are tentative first steps and more will be needed before the convenience and financial advantages of fossil fuels over biomass are removed.