Appl Biochem Biotechnol (2009) 156:525–536
DOI 10.1007/s12010-008-8466-y

Carboxylate Platform: The MixAlco Process Part 1: Comparison of Three Biomass Conversion Platforms

Mark T. Holtzapple · Cesar B. Granda

Received: 23 May 2008 / Accepted: 2 December 2008 /

Abstract To convert biomass to liquid fuels, three platforms are compared: thermochemical, sugar, and carboxylate. To create a common basis, each platform is fed “ideal biomass,” which contains polysaccharides (68.3%) and lignin (31.7%). This ratio is typical of hardwood biomass and was selected so that when gasified and converted to hydrogen, the lignin has sufficient energy to produce ethanol from the carboxylic acids produced by the carboxylate platform. Using balanced chemical reactions, the theoretical yield and energy efficiency were determined for each platform. For all platforms, the ethanol yield can be increased by 71% to 107% by supplying external hydrogen produced from other sources (e.g., solar, wind, nuclear, fossil fuels). The alcohols can be converted to alkanes with a modest loss of energy efficiency (3 to 5 percentage points). Of the three platforms considered, the carboxylate platform has demonstrated the highest product yields.

Keywords Carboxylate platform · Sugar platform · Thermochemical platform · Gasification · Energy efficiency · Yields · Alcohol · Alkanes

Introduction

The major components of lignocellulosic biomass are cellulose and other polysaccharides (collectively represented as $C_6H_{10}O_5$) and lignin (represented as $CH_{1.12}O_{0.377}$). For the purposes of the discussion here, ideal biomass will be defined as 31.7% lignin and 68.3% polysaccharides on an ash-free basis. On a mass basis, this ratio is 2.15:1 polysaccharide/lignin, a composition typical of hardwoods such as hybrid poplar (see Table 1). When expressed according to the given formulas, the molar ratio is 3.93:1 lignin/polysaccharide.

To form products, polysaccharides can be processed thermochemically or biologically under anaerobic conditions. In contrast, lignin is not biologically reactive under anaerobic conditions and can only be processed thermochemically. In ideal biomass, the lignin/

M. T. Holtzapple (✉) · C. B. Granda
Department of Chemical Engineering, Texas A&M University,
College Station, TX 77843-3122, USA
e-mail: m-holtzapple@tamu.edu

Table 1 Typical composition of biomass

Class Example	Herbaceous Switchgrass (Alamo)	Hardwood Hybrid Poplar (DN-34)	Softwood Pine
Carbohydrate/lignin ratio	3.15:1	2.22:1	1.89:1
Lignin	17.56%	25.18%	34.5%
Carbohydrate	55.35%	55.88%	65.3%
Cellulose	30.97%	39.23%	40.4%
Hemicellulose	24.38%	16.65%	24.9%
Reference	NREL Biomass Database [1]	NREL Biomass Database [1]	Klass [2]

polysaccharide ratio is balanced so that when gasified to hydrogen, lignin has sufficient energy to create ethanol from acetic acid that is biologically produced from the polysaccharides. If biomass has more polysaccharides than the ideal ratio, then 100% biological conversion is not necessary; the undigested residue can be gasified and used to upgrade the fermentation products. If biomass has more lignin than the ideal ratio, then extra lignin is available for combustion or conversion to liquid fuels.

The following discussion describes mass and energy balances for various biomass conversion options using ideal biomass as the feedstock.

Mass Balances

Lignin can be gasified with 0.3 equivalence ratio (i.e., it is fed with 0.3 of the oxygen necessary to completely combust the lignin), which converts nearly all the lignin to gaseous products with little char, hydrocarbons, or tar remaining [3]. Further, the carbon monoxide product can be converted to hydrogen using the water–gas shift reaction, as follows:

$$\begin{array}{r} 3.93\,CH_{1.12}\,O_{0.377} + 1.29\,O_2 \rightarrow 3.80\,CO + 0.13\,CO_2 + 2.20\,H_2 \\ \underline{3.80\,CO + 3.80\,H_2O \rightarrow 3.80\,CO_2 + 3.80\,H_2} \\ 3.93CH_{1.12}O_{0.377} + 3.80H_2O + 1.29O_2 \rightarrow 3.93CO_2 + 6H_2. \end{array}$$

The polysaccharides may be converted to ethanol via three methods:

Thermochemical Platform

Gasification of ideal biomass may be visualized as occurring according to the following steps: (1) the lignin is separated from the polysaccharide, (2) the polysaccharide is gasified, (3) the lignin is gasified and shifted to hydrogen, and (4) the resulting gases are passed over a catalyst to yield ethanol, as follows:

$$\begin{array}{r} C_6H_{10}O_5 + H_2O + 1.5O_2 \rightarrow 3CO + 3CO_2 + 6H_2 \\ 3.93CH_{1.12}O_{0.377} + 3.80H_2O + 1.29O_2 \rightarrow 3.93CO_2 + 6H_2 \\ \underline{3CO + 2CO_2 + 12H_2 \rightarrow 2.5H_3CCH_2OH + 4.5H_2O} \\ C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 0.30H_2O + 2.79O_2 \rightarrow 2.5H_3CCH_2OH + 4.93CO_2 \end{array}$$

Spivey and Egbebi [4] describe the production of ethanol from carbon monoxide, carbon dioxide, and hydrogen using a rhodium-based catalyst. Ethanol (and higher alcohols) can be made but, selectively, is difficult. Also, the per pass conversion is very low. Thus, the theoretical yields indicated by the above equation are difficult to achieve in practice.

Sugar Platform

Using the sugar platform to completely convert ideal biomass involves the following steps: (1) carbohydrate polymers are hydrolyzed to sugars using acid or enzyme catalysts, (2) the resulting sugars are fermented to ethanol and carbon dioxide, (3) the remaining lignin is gasified and the resulting gases are shifted to hydrogen, and (4) the hydrogen reduces carbon dioxide to form more ethanol, as follows:

$$\begin{array}{rcl}
C_6H_{10}O_5 + H_2O & \rightarrow & C_6H_{12}O_6 \\
C_6H_{12}O_6 & \rightarrow & 2H_3CCH_2OH + 2CO_2 \\
3.93CH_{1.12}O_{0.377} + 3.80H_2O + 1.29O_2 & \rightarrow & 3.93CO_2 + 6H_2 \\
2CO_2 + 6H_2 & \rightarrow & H_3CCH_2OH + 3H_2O \\
\hline
C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 1.80H_2O + 1.29O_2 & \rightarrow & 3H_3CCH_2OH + 3.93CO_2.
\end{array}$$

Carboxylate Platform

Using the carboxylate platform to completely convert ideal biomass involves the following steps: (1) carbohydrate polymers are hydrolyzed to sugars using enzyme or acid catalysts, (2) the resulting sugars are fermented to acetic acid, (3) the remaining lignin is gasified and the resulting gases are shifted to hydrogen, and (4) the hydrogen reduces the acetic acid to form ethanol, as follows:

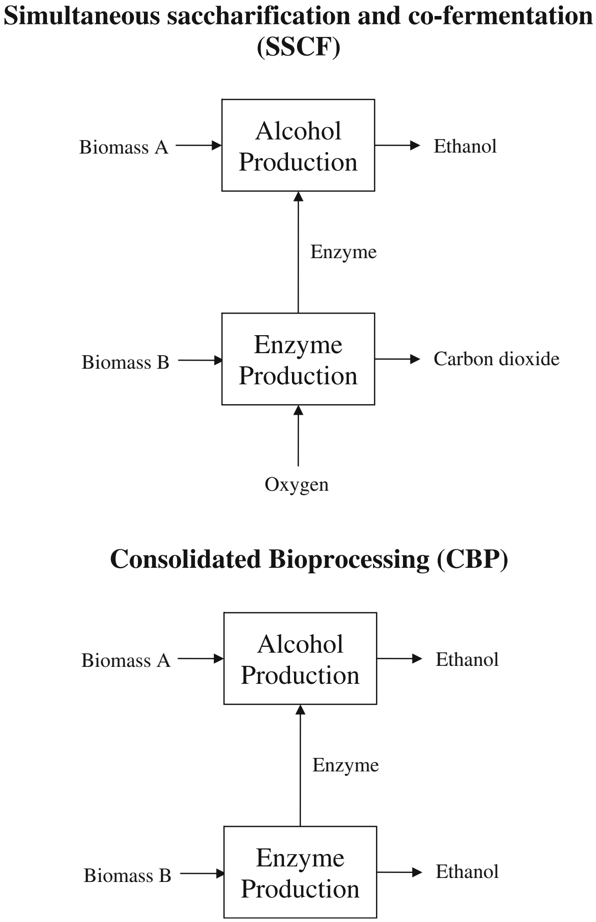
$$\begin{array}{rcl}
C_6H_{10}O_5 + H_2O & \rightarrow & C_6H_{12}O_6 \\
C_6H_{12}O_6 & \rightarrow & 3H_3CCO_2H \\
3.93CH_{1.12}O_{0.377} + 3.80H_2O + 1.29O_2 & \rightarrow & 3.93CO_2 + 6H_2 \\
3H_3CCO_2H + 6H_2 & \rightarrow & 3H_3CCH_2OH + 3H_2O \\
\hline
C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 1.80H_2O + 1.29O_2 & \rightarrow & 3H_3CCH_2OH + 3.93CO_2.
\end{array}$$

Based on the stoichiometry above for ideal biomass, from one mole of sugar, the thermochemical platform produces 2.5 mol of ethanol, whereas the biological routes (sugar and carboxylate platforms) produce 3 mol of ethanol. This results because the gasification partially oxidizes the biomass, which reduces the yields.

From ideal biomass, the maximum potential yield of ethanol is 0.582 kg ethanol per kilogram ash-free biomass (175 gal/ton) using the two biological routes and 0.485 kg ethanol per kilogram ash-free biomass (145 gal/ton) using the thermochemical route.

Consolidated Bioprocessing

As illustrated in Fig. 1, Lynd et al. [5] describes two basic approaches to the biological conversion of biomass to ethanol: (1) simultaneous saccharification and co-fermentation (SSCF) and (2) consolidated bioprocessing (CBP). In the first approach, the majority of the biomass (Biomass A) is anaerobically converted to ethanol using extracellular enzymes that produce hexose and pentose sugars, which are consumed by ethanologenic microorganisms. These enzymes are produced using a small portion of biomass (Biomass B) in an aerobic fermentation, which produces carbon dioxide as a waste product. In the second approach, both processes are operated anaerobically so that ethanol is also produced from enzyme production. (Note that both process steps are envisioned to occur using a single organism in a single vessel, thus they are “consolidated”.) Because process steps are integrated, CBP should have lower capital costs than SSCF. Further, because aerobic gas transfer is not required, CBP should have lower energy consumption than SSCF.



Simultaneous saccharification and co-fermentation (SSCF)

Consolidated Bioprocessing (CBP)

Fig. 1 Biomass conversion using simultaneous saccharification and co-fermentation (*SSCF*) and consolidated bioprocessing (*CBP*)

In anaerobic processing, as enzymes (and cells) are made, the metabolic end-products are useful (e.g., alcohols). In contrast, in aerobic processing, as enzymes (and cells) are made, the metabolic end-products are not useful (carbon dioxide, water). Thus, CBP has the potential for greater ethanol yields than SSCF—the discussion below describes the yield penalty associated with SSCF.

The ratio R is defined as follows:

$$R \equiv \frac{\text{Biomass B}}{\text{Biomass A}} = \frac{\text{Biomass B}}{\text{Enzyme}} \times \frac{\text{Enzyme}}{\text{Biomass A}} = \frac{1}{Y_E} \times L \tag{1}$$

where

$$Y_{\mathrm{E}} = \text{enzyme yield}(\text{g enzyme}/\text{g Biomass B})$$
$$L = \text{enzyme yield}(\text{g enzyme}/\text{g Biomass A}).$$

The enzyme yield Y_{E} is related to enzyme manufacture, whereas the enzyme loading L is related to the saccharification/fermentation and is affected by enzyme activity, the degree of pretreatment, and the desired conversion. Using simple mass balances, it can be shown that the alcohol yield Y_A is:

$$Y_{\mathrm{A}} = Y_{\mathrm{A}}^{\mathrm{o}}\left(\frac{1}{1+R}\right) \tag{2}$$

where

$$Y_A^o = \text{alcohol yield from alcohol production step (g EtOH / g Biomass A)}$$

For example, using *Trichoderma reesei* ZU-02 grown on 40 g/L corn cobs in a 30-m^3 fermentor, Liming and Xueliang [6] achieved an enzyme titer of 5.48 IU/mL with a specific activity of 222.8 IU/g cellulase (Y_E=0.615 g enzyme protein per gram Biomass B). With lime-treated poplar wood, Sierra et al. [7] achieved an overall yield of 82.2% using an enzyme cocktail (cellulase, xylanase, cellobiase) with protein loading of 51 mg enzyme per gram glucan. The glucan content was 0.438 g glucan per gram biomass; therefore, L= 0.022 g enzyme protein per gram Biomass A. Using this example, R=0.0358 and 1/(1+R)= 0.965. Thus, the theoretical yield of ethanol is 3.45% less than can be obtained if the enzyme were made by consolidated bioprocessing.

Based on this example, CBP has only a modest yield advantage over SSCF.

Alcohol to Hydrocarbons

Using zeolite catalysts, alcohols can be dehydrated to alkenes (olefins), which subsequently oligomerize into hydrocarbons such as gasoline, diesel, or jet fuel. For example, the stoichiometry for ethanol is shown below:

$$\begin{array}{l}
4\mathrm{H_3CCH_2OH} \rightarrow 4\mathrm{H_2C=CH_2} + 4\mathrm{H_2O} \\
\underline{4\mathrm{H_2C=CH_2} \rightarrow \mathrm{H_3CCH_2CH_2CH=CHCH_2CH_2CH_3}} \\
4\mathrm{H_3CCH_2OH} \rightarrow \mathrm{H_3CCH_2CH_2CH=CHCH_2CH_2CH_3} + 4\mathrm{H_2O.}
\end{array}$$

When ethanol is converted to hydrocarbon, the mass yield is 60.9%. Thus, if ideal biomass is converted to hydrocarbons via ethanol, the maximum potential yield of hydrocarbons is 0.354 kg hydrocarbon per kilogram ash-free biomass (115 gal/ton) using the two biological routes and 0.295 kg hydrocarbon per kilogram ash-free biomass (95.8 gal/ton) the thermochemical route.

External Hydrogen Source

Fuel yields can be increased using external sustainable hydrogen sources derived from solar (photovoltaic, thermal), wind, nuclear, and reformed fossil fuels (with carbon sequestration). Because of the large quantities available, solar energy is of particular interest.

For a high-yield energy crop (e.g., energy cane, high-yield sorghum), the efficiency of converting sunlight to chemical energy is about 1.2% [assumptions: Southeastern United States. Average annual insolation on a horizontal surface=4.5 kWh/(m^2 day) [8]; crop yield= 45 tonne/(ha year)=20 ton/(acre year); heat of combustion=15.6 MJ/kg)]. A solar collector converts sunlight to hydrogen chemical energy with an efficiency of about 10% to 20% (assumptions: thermal solar collector efficiency=15% to 30%; water electrolysis efficiency= 70%). In the Southwestern desert, the insolation is high [5.5 kWh/(m^2 day)] and land is less expensive. A logical option is to capture solar energy, convert it to hydrogen, and incorporate the hydrogen into biofuels.

External hydrogen can be used to make ethanol from ideal biomass

Thermochemical Route

$$C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 2.79O_2 + 14.80H_2 \rightarrow 4.97H_3CCH_2OH + 7.09H_2O.$$

Biological Route

$$C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 1.29O_2 + 11.80H_2 \rightarrow 4.97H_3CCH_2OH + 4.09H_2O.$$

Regardless of the route, the theoretical yield is 0.964 kg ethanol per kilogram ash-free biomass (289 gal/ton), although the thermochemical route requires more hydrogen, and therefore more land area.

External hydrogen can be used to make hydrocarbons from ideal biomass.

Thermochemical Route

$$C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 2.79O_2 + 16.02H_2 \rightarrow 1.24H_3C(CH_2)_6CH_3 + 12.06H_2O.$$

Biological Route

$$C_6H_{10}O_5 + 3.93CH_{1.12}O_{0.377} + 1.29O_2 + 13.02H_2 \rightarrow 1.24H_3C(CH_2)_6CH_3 + 9.06H_2O.$$

The theoretical yield is 0.596 kg hydrocarbon per kilogram ash-free biomass (194 gal/ton).

Energy Balances

The higher heat of combustion for cellulose and lignin is 17.6 and 29.5 MJ/kg, respectively [9, 10]; thus, for ideal biomass, the higher heat of combustion is 21.4 MJ/kg. The higher heat of combustion for ethanol is 29.785 MJ/kg; therefore, from ideal biomass, the maximum theoretical energy efficiencies of the biological and thermochemical routes are 81.0% and 67.5%, respectively.

Thus far, the discussion has focused on two-carbon chemistry (ethanol, acetic acid). It is possible to convert biomass to fuels with different carbon numbers. The higher heat of combustion [11] as a function of carbon number C in a given fuel is shown below:

$$\Delta H_{acid} = -649.4\,C + 411.4 \qquad \text{(carboxylic acid)} \tag{3}$$

$$\Delta H_{alcohol} = -650.1\,C - 72.03 \qquad \text{(alcohol)} \tag{4}$$

$$\Delta H_{alkane} = -645.0\,C - 290.5 \qquad \text{(linear alkanes)} \tag{5}$$

where the higher heat of combustion is in kilojoules per mole. The higher heat of combustion for hydrogen and carbon monoxide [12] follows:

$$\Delta H_{CO} = -282.99\ \mathrm{kJ/mol}$$
$$\Delta H_{H2} = -285.84\ \mathrm{kJ/mol}.$$

The efficiency of producing higher alcohols from carbon monoxide and dioxide is described below:

CO to Alcohol

$$2CO + 4H_2 \rightarrow H_3CCH_2OH + H_2O \qquad \text{(Ethanol)}$$
$$3CO + 6H_2 \rightarrow H_3CCH_2CH_2OH + 2H_2O \qquad \text{(Propanol)}$$

$$\eta = \frac{\Delta H_{\text{alcohol}}}{C\Delta H_{\text{CO}} + 2C\Delta H_{\text{H}_2}}. \tag{6}$$

CO_2 to Alcohol

$$2CO_2 + 6H_2 \rightarrow H_3CCH_2OH + 3H_2O \qquad \text{(Ethanol)}$$
$$3CO_2 + 9H_2 \rightarrow H_3CCH_2CH_2OH + 5H_2O \qquad \text{(Propanol)}$$

$$\eta = \frac{\Delta H_{\text{alcohol}}}{3C\Delta H_{\text{H}_2}}. \tag{7}$$

Figure 2 shows that the efficiency is the same regardless of whether CO or CO_2 is used. The efficiency decreases with increasing carbon number.

The efficiency of hydrogenating carboxylic acids to alcohols and their subsequent conversion of alcohols to hydrocarbons (alkanes) are described below.

Carboxylic Acid to Alcohol

$$H_3CCOOH + 2H_2 \rightarrow H_3CCH_2OH + H_2O \qquad \text{(Ethanol)}$$
$$H_3CCH_2COOH + 2H_2 \rightarrow H_3CCH_2CH_2OH + H_2O \qquad \text{(Propanol)}$$

$$\eta = \frac{\Delta H_{\text{alcohol}}}{\Delta H_{\text{acid}} + 2\Delta H_{\text{H}_2}}. \tag{8}$$

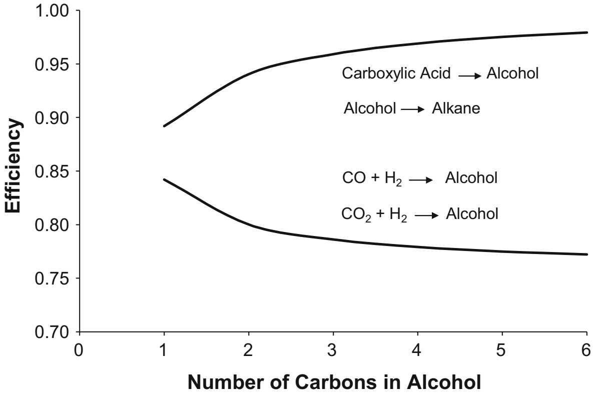


Fig. 2 Theoretical energy efficiency of alcohol and alkane production depending upon number of carbons

Alcohol to Octane

$$\begin{array}{lr} 4H_3CCH_2OH + H_2 \rightarrow H_3C(CH_2)_6CH_3 + 4H_2O & \text{(Ethanol)} \\ 2H_3C(CH_2)_2CH_2OH + H_2 \rightarrow H_3C(CH_2)_6CH_3 + 2H_2O & \text{(Butanol)} \end{array}$$

$$\eta = \frac{\Delta H_{\text{octane}}}{(8/C)\Delta H_{\text{alcohol}} + \Delta H_{H_2}}. \tag{9}$$

Alcohol to Dodecane

$$\begin{array}{lr} 6H_3CCH_2OH + H_2 \rightarrow H_3C(CH_2)_{10}CH_3 + 6H_2O & \text{(Ethanol)} \\ 4H_3CCH_2CH_2OH + H_2 \rightarrow H_3C(CH_2)_{10}CH_3 + 4H_2O & \text{(Propanol)} \\ 3H_3C(CH_2)_2CH_2OH + H_2 \rightarrow H_3C(CH_2)_{10}CH_3 + 2H_2O & \text{(Butanol)} \end{array}$$

$$\eta = \frac{\Delta H_{\text{dodecane}}}{(12/C)\Delta H_{\text{alcohol}} + \Delta H_{H_2}}. \tag{10}$$

Figure 2 shows that the efficiency is the same regardless of whether carboxylic acids are converted to alcohols or alcohols are converted to alkanes. The efficiency increases with increasing carbon number.

The product of the two curves shown in Fig. 2 is constant (75%); thus, the efficiency of converting CO or CO_2 to alkanes is the same regardless of the number of carbons in the intermediate alcohol.

Discussion

Table 2 shows the yields of liquid fuels from ideal biomass, which are summarized from the previous discussion. Column 1 shows the theoretical ethanol yields from ideal biomass from polysaccharides only. Column 2 shows the theoretical ethanol yields from ideal

Table 2 Yields of liquid fuels from biomass (gal/ton ash-free biomass)

	Theoretical (ideal biomass)					Literature (real biomass)		
External H_2	No			Yes		No		Compared to theoretical
Lignin converted to liquid fuel	No	Yes				No	Yes	
Column number	1	2	3	4	5	6	7	
Product	Ethanol	Ethanol	Alkane	Ethanol	Alkane	Alcohol		(%)
Thermochemical platform	–	145	95.8	289	194	–	80.1[a]	55.2
Sugar platform								
CBP	117	175	115	289	194	100[b]	–	85.5
SSCF	113	169	111	279	187	65[c]	–	55.5
Carboxylate platform	–	175	115	289	194	–	127[d]	72.6

[a] Mixed alcohols with 73% ethanol [13] expressed as ethanol equivalents [14]

[b] Expected [15]

[c] [13]

[d] Ethanol equivalents [16]

biomass using both the polysaccharides and lignin. Column 3 shows the theoretical yield resulting from the conversion of ethanol (Column 2) into alkanes. Column 4 shows the theoretical ethanol yields from ideal biomass by converting all the biomass carbon to ethanol and employing an external hydrogen source. Column 5 shows the yield resulting from the conversion of ethanol (Column 5) into alkanes. Columns 6 and 7 show actual alcohol yields taken from the literature. The last column compares the literature yields to the theoretical limits.

From Table 2, the following observations may be made:

- Column 1 vs. 2—Converting the lignin in addition to the polysaccharides raises fuel yields by 50%.
- Columns 2 and 3—The thermochemical platform has about 17% lower yields than the biological platforms (sugar or carboxylate) because the biomass polysaccharides are partially combusted.
- Columns 4 and 5—When an external source of hydrogen is provided, the theoretical yields of liquid fuels are the same for the thermochemical and biological platforms because any carbon lost in the partial combustion can be recovered from hydrogen addition.
- Columns 1 to 5—The SSCF yields are about 3.5% less than the CBP yields because a portion of the biomass is lost to aerobic enzyme production.
- Column 2 vs. 4—Providing an external source of hydrogen raises ethanol yields by 99% (thermochemical) and 65% (biological).
- Column 3 vs. 5—Providing an external source of hydrogen raises alkane yields by 103% (thermochemical) and 69% (biological). The extra increase in comparison to the ethanol yields increase comes from the fact that double bonds are hydrogenated ending up with saturated alkanes rather than olefins.
- Column 1 vs. 6—CBP is projected to have ethanol yields about 85 to 90% of theoretical, but this has not yet been demonstrated. SSCF has achieved about 58% of theoretical.
- Column 2 vs. 7—Thermochemical has achieved 55% of theoretical. The carboxylate platform has achieved about 73% of theoretical.
- Column 7—Compared to the other platforms, the carboxylate platform has achieved the highest potential alcohol yield. (Note that so far, conversion to carboxylate salts has been demonstrated in the laboratory. The alcohol yield shown assumes that the subsequent chemical steps are 97% efficient.)

Table 3 shows the energy efficiency of the various platforms. Column 1 shows the theoretical energy efficiency of the biological step where polysaccharide is converted to ethanol (sugar platform) or carboxylic acid (carboxylate platform). Columns 2 and 3 show the theoretical energy efficiency of converting both polysaccharides and lignin to ethanol and alkanes, respectively. Columns 4 and 5 show the same conversions, but with supplemental hydrogen from an external source.

From Table 3, the following observations may be made:

- Column 1—All the biological conversion steps are over 90% efficient with CBP being the most efficient (96.3%) and SSCF being the least efficient (92.9%).
- Columns 2 to 5—Thermochemical is the least efficient platform when both polysaccharides and lignin are converted to ethanol. (Note that although liquid fuel yields are lower, much of the inefficiency results in high-temperature heat, which can be converted to electricity.)
- Column 1 vs. 2—Gasification of lignin increases product yields (Table 2), but lowers efficiency.

Table 3 Theoretical efficiency of liquid fuels from ideal biomass (%)

External H_2	No			Yes	
Column	1 Biological step	2 Ethanol product	3 Alkane product	4 Ethanol product	5 Alkane product
Thermochemical platform	–	67.5	63.7	73.2	70.0
Sugar platform					
CBP	96.3[a]	81.0	76.4	80.7	76.8
SSCF	92.9[a]	78.2	73.7	77.9	74.2
Carboxylate platform	93.4[b]	81.0	76.4	80.7	76.8

[a] Ethanol product

[b] Acetic acid product

- Column 2 vs. 3—Conversion of alcohols to alkanes reduces the efficiency slightly (3 to 5 percentage points), but yields a product with higher energy density and greater compatibility with the current fuel infrastructure.
- Columns 2 and 3 vs. Columns 4 and 5—Providing an external source of hydrogen increases the efficiency of the thermochemical platform, but has almost no effect on the efficiency of the biological platforms (sugar and carboxylate).

Table 4 shows the percentage of the energy input supplied from an external source of hydrogen for the various scenarios discussed thus far. Depending upon the scenario, the external hydrogen source can provide 39% to 48% of the energy in the liquid fuel.

The Case for the Carboxylate Platform

The carboxylate platform has the following advantages:

- It has demonstrated the highest product yields in the literature.
- In the carboxylate platform, gasified lignin is utilized by conversion to hydrogen, which is efficiently accomplished through the water–gas shift reaction. In contrast, in the other platforms, gasified lignin is utilized by conversion to carbon-containing molecules (e.g., alcohols or alkanes), which has low yields in practice (see column 7, Table 2).
- Biomass can be converted to carboxylic acids using a mixed culture of microorganisms, which eliminates the need for aseptic processing conditions.

Table 4 Theoretical energy supplied from external hydrogen (%)

External H_2	No		Yes	
Product	Ethanol	Alkane	Ethanol	Alkane
Thermochemical platform	0	0	45.4	47.4
Sugar platform				
CBP	0	0	39.9	42.3
SSCF	0	0	39.9	42.3
Carboxylate platform	0	0	39.9	42.3

- Using a mixed culture of microorganisms allows nearly all non-lignin biomass components (e.g., polysaccharides, pectins, fats, proteins) to be biologically converted, which is more energy efficient than thermochemical conversion.
- The carboxylate platform is an example of CBP. Because all enzymes and cells are made anaerobically, metabolic end-products (i.e., carboxylic acids) are useful.
- Using a mixed culture of microorganisms allows enzymes and cells to be recycled and metabolized to additional useful end-products (i.e., carboxylic acids). This is not possible with pure cultures.
- To take advantage of the energy content in lignin, the carboxylate platform requires that synthesis gas be converted to hydrogen, which is an easy catalytic step. In contrast, the other platforms require that gases (carbon dioxide, synthesis gas) be converted to ethanol, which is a challenging catalytic step.

The advantages of the carboxylate platform have been recognized [17, 18] (Angenent L., Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis. Campus Box 1180, One Brookings Drive, St. Louis, MO 63130, personal communication; Flatt and van Walsum, manuscript in preparation), all of whom are pursuing active research projects in this area.

Conclusion

To convert biomass to liquid fuels, three platforms have been considered: (1) thermochemical, (2) sugar, and (3) carboxylate. Because all the biomass must be partially oxidized, thermochemical is the least efficient conversion method and has the lowest yields. Complete utilization of biomass requires that the energy of the lignin fraction be converted to liquid fuels. The sugar and carboxylate platforms employ biological processes that cannot utilize lignin, so these platforms require that the undigested lignin residue be gasified. In the sugar platform, the gasified lignin must be converted to liquids directly, which is difficult. In contrast, the carboxylate platform requires that the gasified lignin be converted to hydrogen, which is an efficient and well-developed conversion technology.

Most biomass conversion technology focuses on alcohols, primarily ethanol. Alcohols can be converted to alkanes with minor losses of energy. Given the higher energy density of alkanes, and their compatibility with the current infrastructure, this is an attractive option. If the ultimate objective is to make alkanes from alcohols, it does not matter how many carbons are in the intermediate alcohols—the overall efficiency is the same.

When converting gasified biomass directly to liquid fuels, the most efficient product is methanol (84%), whereas the higher alcohols have a lower efficiency (77% to 80%). If the gasified biomass is converted to alkanes, the overall efficiency is lower (75%).

The efficiency of converting sunlight to plant matter is fairly low (~1%). For the same chemical energy production, less land area is required if sunlight is converted to hydrogen (10% to 20% efficiency). This external source of hydrogen can be incorporated into the biofuel products and provide 39% to 48% of the energy content in the biofuel.

The carboxylate platform has the highest achieved product yields of the three. The conversion of the biodegradable portions of the biomass can be performed with a mixed culture of microorganisms, thus eliminating the need for aseptic fermentation. Mixed-culture fermentations digest all non-lignin biomass components, including cellulose, hemicellulose, pectin, fats, and proteins. The undigested portions of the biomass can be gasified to make hydrogen, which converts the carboxylic acids to alcohols or alkanes.

References

1. NREL Biomass Database. http://www1.eere.energy.gov/biomass/feedstock_databases.html.
2. Klass, D. L. (1998). *Biomass for renewable energy, fuels, and chemicals* p. 81. San Diego: Academic.
3. Reed, T. B. (1981). *Biomass gasification: Principles and technology* p. 10. Park Ridge, NJ: Noyes Data Corporation.
4. Spivey, J. J., & Egbebi, A. (2007). Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society Review*, *36*, 1514–1529.
5. Lynd, L. R., van Zyl, W. H., McBride, J. E., & Laser, M. (2005). Consolidated bioprocessing of cellulosic biomass: An update. *Current Opinion in Biotechnology*, *16*, 577–583.
6. Liming, X., & Xueliang, S. (2004). High-yield cellulase production by *Trichoderma reesei* ZU-02 on corn cob residue. *Bioresource Technology*, *91*(3), 259–262.
7. Sierra, R., Granda, C., & Holtzapple, M. T. (2008). Short-term lime pretreatment of poplar wood. *Biotechnology Progress* (in press).
8. NREL .rredc.nrel.gov/solar/old_data/nsrdb/redbook/atlas/serve.cgi.
9. Holtzapple, M. T. (2003a). Cellulose. In B. Caballero, L. C. Trugo, & P. M. Finglas (Eds.), *Encyclopedia of food science, food technology, and nutrition*(2nd ed.). London: Academic.
10. Holtzapple, M. T. (2003b). Lignin. In B. Caballero, L.C. Trugo, & P.M. Finglas (Eds.), *Encyclopedia of food science, food technology, and nutrition* (pp. 3535–3542, 2nd ed.). London: Academic.
11. Weast, R. C. (1977). *CRC handbook of chemistry and physics* (58th ed.). West Palm Beach, FL: CRC.
12. Felder, R. M., & Rousseau, R. W. (1986). Elementary principles of chemical processes, 2nd ed. Wiley, New York.
13. Ferrel, J., US DOE Biomass Program (2006). http://www.ars.usda.gov/SP2UserFiles/Program/307/DOEBiomassProgram.pdf.
14. Aden, A. (2005). Technical and economic feasibility of mixed alcohols fuel production from biomass-derived syngas. *AiChE National Meeting*, November 3rd.
15. Lynd, L. R., & Wang, M. Q. (2004). A product-nonspecific framework for evaluating the potential of biomass-based products to displace fossil fuels. *Journal of Industrial Ecology*, *7*(3–4), 117–146.
16. Agbogbo, F. K., & Holtzapple, M. T. (2007). Fixed-bed fermentation of rice straw and chicken manure using a mixed culture of marine mesophilic microorganisms. *Bioresource Technology*, *98*(8), 1586–1595. doi:10.1016/j.biortech.2006.06.021.
17. Eggeman, T., & Verser, D. (2006). The importance of utility systems in today's biorefineries and vision for tomorrow. *Applied Biochemistry and Biotechnology*, *129–132*, 361–381.
18. Granda, C., & Holtzapple, M. (2008). Biorefineries for solvents: The MixAlco process. In J. Wall, C. Harwood, & A. Demain (Eds.), *Bioenergy*. Washington, DC: ASM.