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The Industrial Playing Field for the Conversion of Biomass to Renewable Fuels and Chemicals

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1.1
Introduction

The world is changing its chemistry backbone. In recent years, it has become clear that the feedstocks of choice for the chemical industry can no longer be just petrochemical-based and that alternatives from biomass will need to become readily available in the near future. This has been driven not only by rising fuel prices and the location of much of the petroleum reserves but also the developing insights as to the effects of additional CO_2 on the changing climate of our planet. Many countries are now pursuing the development of new technology for the conversion to fuels and chemicals of renewable feedstocks from biomass that can be grown locally and harvested, such as wood, agricultural crops, algae, municipal waste and animal residue.

In this book we will focus in great detail, from an industrial perspective, on chemical and process technology routes, and the many challenges for these new platform chemicals, their production routes and their potential compared to biological and traditional oil-based technologies. In this chapter an overview of the most important industrial research efforts and strategies is given. The change to a biomass-based economy faces several challenges as the chemistries involved and new platform chemicals that will become available can differ radically from those used for petroleum feedstocks. In addition, it is clear to all involved that a considerable research effort still lies ahead of us.

In this, it is exemplary to consider the petrochemical industry. It has taken several decades to develop technology for the conversion of crude oil and gas into transportation fuels and chemicals and this research effort is still ongoing. In contrast to the exploration of crude oil and the production of fuels and chemicals, which typically involve cracking of carbon–carbon bonds, heterogeneous acid catalysis and hydrotreatment, the renewable feedstocks require a new collection and distribution system and the conversion of wet, highly functional carbohydrates into products that will ideally be compatible with existing refinery operations. As a result, new catalysis and biology need to be developed to convert these oxygenated feedstocks to useful products.

Catalytic Process Development for Renewable Materials, First Edition. Edited by Pieter Imhof and
Jan Cornelis van der Waal.

1.2
The Renewables Arena

Many companies are active in the emerging renewables arena. In this chapter, several of the large multinational and several of the smaller start-up companies will be discussed in more detail. A nice way to identify the key-players based in the field is by looking at the yearly Biofuels Digest polls among its readers and the list of the top 50 companies that its readers deem most active in the renewable fuels and chemicals area [1]. The top 50 companies from the 2010–2011 survey are shown in Table 1.1. It is also interesting to note that the focus of these companies differs both in feedstocks used and in products made, exemplifying that the use of biomass is a general concept and is in good agreement with environmental effort to create biodiverse, sustainable agricultural landscapes.

An alternative way is to look at the most promising bio-renewable platform chemicals derived from the various processes to see which companies have either production capacity already or have reported development of new processes. Table 1.2 shows a list of products with strong growth potential in the chemical industries and some promising ones that are well advanced in the pipeline [2].

The companies shown in Tables 1.1 and 1.2 also reveal the broad and diverse interest in biorenewable fuels and chemicals. The effort is carried by both established

Table 1.1 The top 50 bioenergy companies, compiled by Biofuels Digest 2010–2011.

1	Amyris	26	Algenol
2	Solazyme	27	ZeaChem
3	POET	28	PetroAlgae
4	LS9	29	Neste
5	Gevo	30	Synthetic Genomics
6	DuPont Danisco	31	LanzaTech
7	Novozymes	32	Iogen
8	Coskata	33	OriginOil
9	Codexis	34	Range Fuels
10	Sapphire Energy	35	ExxonMobil
11	Virent	36	Cargill
12	Mascoma	37	SG Biofuels
13	Ceres	38	Butamax
14	Cobalt Technologies	39	Terrabon
15	Honeywell's UOP	40	Cosan
16	Enerkem	41	Verenium
17	BP Biofuels	42	Waste Management
18	Genencor	43	IneosBio
19	Petrobras	44	Dynamic Fuels
20	Abengoa Energy	45	Fulcrum Bioenergy
21	Qteros	46	KL Energy
22	Joule Unlimited	47	KiOR
23	Shell	48	Chevron
24	Bluefire Renewables	49	Monsanto
25	Rentech	50	Inbicon

Table 1.2 Production of platform chemicals [2].

Cn	Products with strong growth potential		Biobased chemicals in the pipeline	
	Chemical	**Company**	**Chemical**	**Company**
1	Methanol	BioMCN, Chemrec	Formic acid	Maine BioProducts
2	Ethylene	Braskem, DOW, Songyuan Ji'an Biochemical	Ethyl acetate	Zeachem
	Ethanol	Many	Glycolic acid	Metabolix Explorer
	Ethylene glycol	India Glycols Ltd, Greencol Taiwan	Acetic acid	Wacker
3	Lactic acid	Purac, NatureWorks, Galactic	Acrylic acid	Cargill, Perstorp, OPXBio, DOW
	Glycerol	Many	Propylene	Braskem
	Epichlorohydrin	Solvay, DOW	3-Hydroxypropionic acid	Cargill
	1,3-Propanediol	DuPont/Tate&Lyle	n-Propanol	Braskem
	Ethyl lactate	Vertec BioSolvents		
	Propylene glycol	ADM	Isopropanol	Genomatica
4	n-Butanol	Cathay Industrial Biotech	1,4-Butanediol	Genomatica
	iso-Butanol	Butamax, Gevo	Methyl methacrylate	Lucite
	Succinic acid	DSM, BioAmber, Myriant		
5	Furfural	Many	Itaconic acid	Itaconix
	Xylitol	Lenzing	Isoprene	Goodyear/Genencor, Amyris
			Levulinic acid	Maine BioProducts, Avantium, Segetis
6	Sorbitol	Roquette, ADM	Adipic acid	Verdezyne, Rennovia, BioAmber, Genomatica
	Isosorbide	Roquette	FDCA	Avantium
	Lysine	Draths	Glucaric acid	Rivertop, Genencor
	Caprolactam	DSM		
N	PHA	Telles	*para*-Xylene	Gevo, Draths, Annellotech, Virent
	Fatty acid derivatives	Croda	Farnesene	Amyris

large multinationals and young inventive start-ups, but the diversity is also clear in other aspects. For example, renewable fuels are obtained from different feedstocks, such as algae, oils, and carbohydrates to challenging ones such as lignin, lignocellulosics and municipal solid wastes. Clearly, with such a broad range of feedstocks many different technologies need to be developed and applied. Currently fermentation of carbohydrates to ethanol is by far the biggest process, but other fermentations, like Gevo's butanols and Amyris's Farnesenes, are now commercialized. However, chemical catalysis will quickly pick up from there and convert the fermented products further. The announcement of The Coca Cola Company [3] of collaboration with Gevo, Virent and Avantium to develop 100% biobased beverage bottles is based on three different catalytic technologies.

One thing the tables above do not reflect well is the considerable impact that existing, well-established technologies have in the renewable area. The fermentation of carbohydrates to alcoholic beverages (6.1 l of pure alcohol per person aged over 15 year worldwide or 32 Mtonne per year total [4]), and the use of vegetable oils that can be saponified to soaps, emulsifiers and other chemicals (around 14% of world production of vegetable oils or an equivalent of 16.8 Mtonne per year [5]).

When each entry in Tables 1.1 and 1.2 is categorized by feedstock use, product made, type of processing, and geographic location, one can draw certain conclusions as to the state and the direction for the current chemicals from renewables efforts. In this analysis, no differentiation between company size and/or development/maturity state of the process is made and the numbers presented are based purely on the number of companies involved. With respect to the geographic spread of companies involved in the renewable areas (see Figure 1.1), it is clear that the United States of America, with two-thirds of the companies being located there, is leading. At first sight, the contribution of Asia appears to be small. However, many of the larger industrial conglomerates are collaborating very actively with smaller start-up companies all over the world. In addition, this survey did not include the already existing biorenewable efforts in which Asia has a long-standing tradition, especially palm oil and alternative sugar crops, such as rice and tapioca, which offer great potential as feedstocks for biorenewable fuels and chemicals (Figure 1.1).

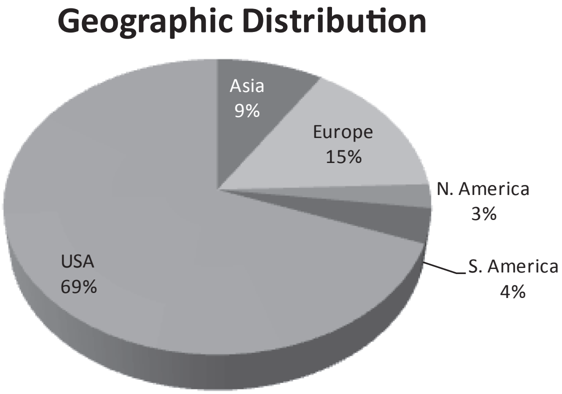


Figure 1.1 Geographic distribution of companies in the renewable area.

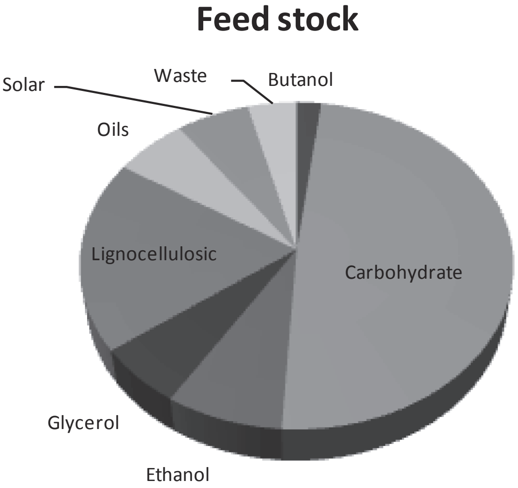


Figure 1.2 Distribution of feedstock use in the renewable area by number of companies. Carbohydrates refer to readily available sugars (glucose, fructose, sucrose, xylose). Oils refer to vegetable oils.

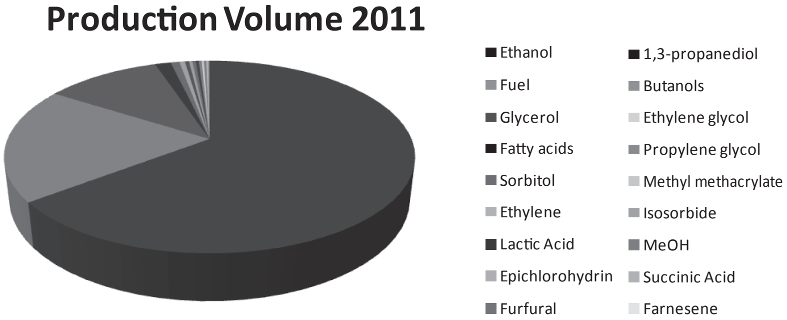


Figure 1.3 Distribution of renewable products made scaled to reported production volume. The production volume in $\mathrm{kt\,a^{-1}}$ for the five largest products is also shown.

With respect to the biomass feedstock used, it is clear from Figure 1.2 that carbohydrates, including lignocellulosics, make up 74% of the starting material; even more if one considers that ethanol and butanol as the starting product in most cases originate from carbohydrates by an earlier fermentation process. The concept of using intermediates derived from biomass is called secondary-derived biobased platform chemicals. Ethanol and butanol, from fermentation of sugars, are examples, but it is not restricted to this. Dohy [2] identified several groups, that is, biogas, syngas (Chapter 10) and H_2, pyrolysis oils (Chapter 8), vegetable oils (Chapter 7), lignin (Chapter 9) and the C5 and C6 sugars (Chapters 4 and 8). Fermentation (Chapters 3 and 6) and catalytic conversion of the latter two (Chapter 4) gives rise to an even more diverse group of products, as was identified by Werpy [6] (Figure 1.2). In addition the use of CO_2 as feedstock is addressed in Chapter 11.

In Figure 1.3 the distribution of renewable products is shown. From this figure it is clear that the products industry currently still focuses on ethanol and fuel

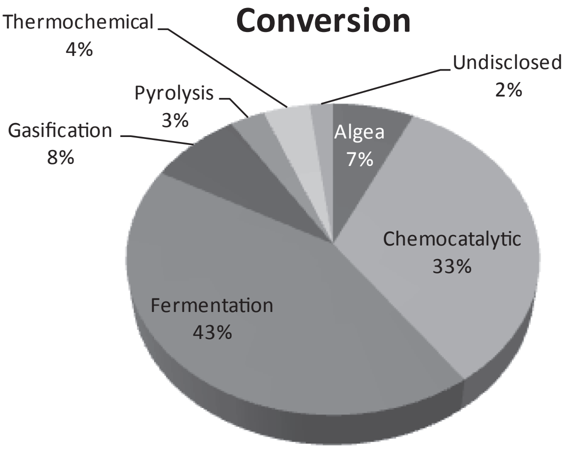


Figure 1.4 Distribution by type of conversion process used by number of companies.

production. There is a strong correlation with the size of the company and the production of these two main products. Smaller, often venture capital backed companies tend to focus on drop-in solutions, hence ethanol, biodiesel and other fuels. This probably reflects the perceived reduced risk profile for these drop-in products. The established low-key technology needed, and the small production volumes. However, one should consider that obtaining a market share can still constitute a high risk since one is competing against almost fully optimized processes employing depreciated capital.

It is also very instructive to consider the type of process used to produce the biorenewable product. From Figure 1.4 it is clear that the most commonly used type of processing is a biological type of conversion, that is fermentative and/or enzymatic (43 processes, 52.1 Mtonne per year) or algae (7 processes, 0.2 Mtonne/year). Not surprisingly, a very strong correlation with ethanol can be observed here. Similarly, chemocatalytic processes are dominated by the FAME (fatty acid methyl ester) biodiesel production. If these two fuel products are excluded from the analysis, the contribution of fermentative processes to the other products is still very high (42%). The remainder of the processes used are bio-renewable chemicals divided between thermal processes and chemocatalytic processes. Especially, the overall low usage of chemocatalytic routes today is surprising as this is in stark contrast with current day petro-based chemicals production where almost all process and products involve catalysis at some point.

It is also refined from our data that the more specialized products in the graph are generally produced by larger multinationals which have the financial backbone and market outlets, or by small companies that have access to a unique technology, often fermentative/enzymatic in nature. Both parties have found each other and many collaborations and joint ventures have since been announced. An overview of these collaborations is given in Table 1.3.

Table 1.3 Overview of efforts, collaborations and joint ventures of some large, multinational oil companies mid-2011.

Company	Field	Partner company	Since	Status
Abengoa energy	Ethanol (carbohydrate)	–		3 plants
BP	Algae	Martek Biosciences	2009	
	Butanol	Butamax	2003	
	Ethanol (cellulosic)	JV with Dupont	2009	
	Diesel (oil seeds)	Verenium (acquired)	2006	
		TERI		
Chevron	Algae	Solazyme	2008	
	Diesel (oil seeds)	Bioselect	2007	1 plant
	Ethanol (carbohydrate)	LS9	2011	
ConocoPhilips	Algae	Colorado Center for	2007	
	Biofuel research	Biorefining and Biofuels	2007	2 plants
	Diesel (oils seeds)	Iowa State University	2007	
		Tyson Foods		
DuPont	Butanol	Butamax	2003	
		JV with BP		
Exxon	Algae	Synthetic Genomics, Inc.	2009	
	Biodiesel	–	2008	
	Gasification	–	2008	
Honeywell UOP	Pyrolysis	Envergent	2008	
		JV Ensyn Corp.		
JX Nippon oil	Diesel (oil seeds)	JV Petronas, Toyota		Pilot
Mitsubishi	Methyl methacrylates	Lucite (acquired)	2008	
Mitsui	Ethanol (carbohydrate)	Dow, Hitachi Zosen	2011	
	Ethanol (syngas)	LanzaTech	2011	
	Ethanol (waste)	Sime Darby	2010	
	Succinic acid	BioAmber	2011	
Neste	Diesel (oil seeds)			2 plants
Petrobras	Ethanol (carbohydrate)	Biocombustível		7 plants
	Diesel (oil seeds)	Biocombustível	2010	1 plant
	Diesel (oil seeds)	BSBIOS	2009	
	Algae	Galp Energia		
	Biofuel (cellulosic)	JV with Eni		
		BiChem		
Sinopex	Diesel (oil seeds)	JV CNOOC, Novozymes		
Shell	Valeric esters	–	Ended 2011	
	Algae	Cellana	Ended 2009	1 plant
	Gasification	Choren	Ended 2009	
	Ethanol (cellulosic)	Iogen	2010	
	Ethanol (carbohydrate)	Raizen	2009	
	Ethanol (waste)	JV with Cosan	2006	
	Cellulosic to fuel	Codexis	2010	
		Virent, Cargill		
Total	Ethanol (carbohydrate)	Coskata	2010	

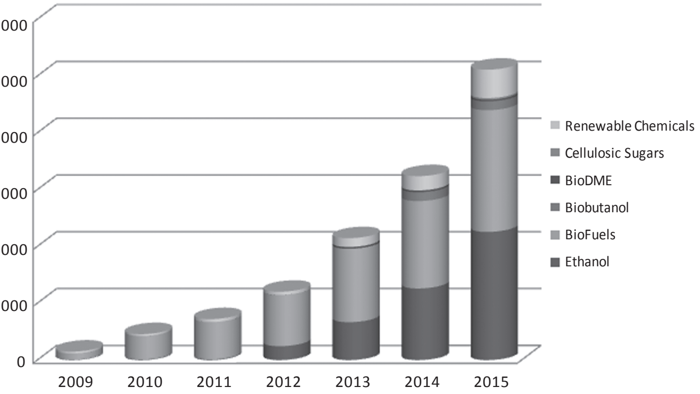


Figure 1.5 Prognoses of growth in biorenewable products in total kt a^{-1} by new technologies [1].

Today's status of the biorenewable fuels and chemicals world is one of direct drop-in replacements and thus strongly tied to fermentation of sugars to ethanol and transesterification of vegetable oils to biodiesel. What is also clear from our survey is that the use of secondary derived biobased platform chemicals is still very limited, suggesting that considerably more effort will be needed in this area for the chemical industry to be able to offer a full biomass-to-product portfolio. In Figure 1.5 the projected cumulative production volume of new biorenewable chemicals and fuels processes, based on announced production volumes employing novel technologies, is shown. The total production volume of 5.1 MTonne per year, however, is still small compared to the current total production volume for ethanol and FAME in 2010, which exceeded 80 Mtonne per year.

Though the advance of new biobased products seems small, it should be realized that these are only the front-runners of a whole new generation of materials. Many of the technologies are not yet mature enough for commercial (pilot-) plant production. At least 25 research efforts in particular bio-renewable chemicals are reported for the 2011–2015 period. In Figure 1.6 these 25 bio-renewable chemicals are shown, with the number of independent research efforts for each identified. Clearly, ethanol and fuels are still the biggest contributors, but it is without doubt that an impressive number of widely diverse chemicals will become available in the near future (Figure 1.6).

The world today is seeing more and more processes that are using bio-renewables. Certain production routes are well-established with large production volumes, such as the traditional fermentation of sugars to ethanol or the transesterification of fatty acids to FAME. However, it is clear that on the horizon a diverse spectrum of molecules will become available. Unlike the current petrochemical-based chemicals industries, which use almost exclusively chemocatalytic and thermal processes, the role of fermentation and enzymatic conversions will be much more marked in the bio-refinery of the future. Still, we have a long way to go. Today, processes are focused on drop-in replacements or on the conversion of biomass

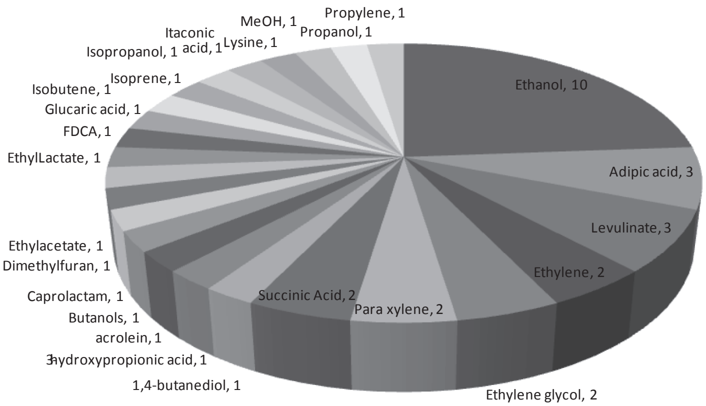


Figure 1.6 Announced research efforts until 2015 in new biobased renewable chemicals. The number in each pie indicates the number of companies researching and/or producing the renewable chemicals.

in secondary derived biobased platform chemicals. Future research will most likely start to focus on further conversions of these platform chemicals, and will make use of technology closer to the catalytic processes currently in place.

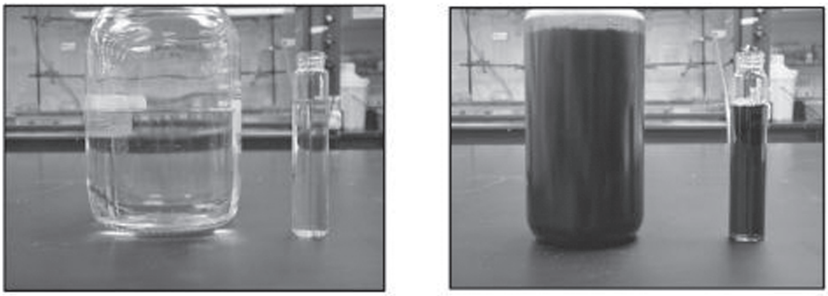
In the next two sections recent developments in the renewable fuels and in the renewable chemicals areas will be discussed. Although most players clearly state what their aim is, it is also clear that an overlap exists between the two areas. Where needed the effort of such players is divided over the two sections.

1.3
Renewable Fuels

The eventual transition from petroleum-based transportation fuels to renewable fuels provides a huge boost for new catalysis and process research. The existing renewable gasoline market is entirely dominated by ethanol, with butanol or its isomers as an emerging alternative, both of which are obtained by fermentation of carbohydrates. The existing renewable diesel market is dominated almost entirely by the fatty acid ester derived products. As was already noted in the introduction, most of the producers of these biofuels appear to be small companies, but one should realize that most large multinationals have active collaborations or joint ventures with these companies. In the previous section an overview of the efforts of multinationals in the biofuels area was given (Table 1.3). From this list it is clear that almost all large oil companies embrace the biofuel concept. However, other than production in first generation biofuels, that is ethanol and FAME diesels, most research efforts are directed through collaboration with new, smaller enterprises.

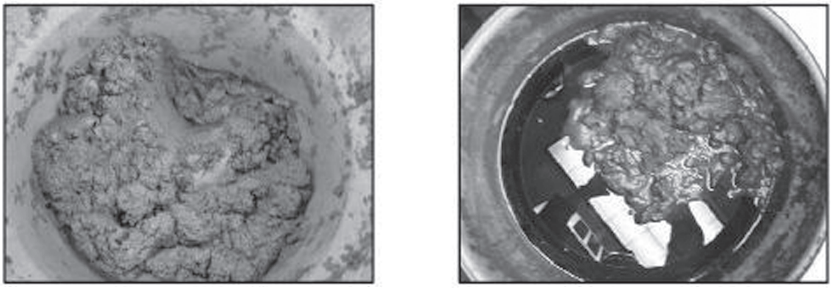
It has also been recognized that the use of food feedstocks is not desirable in the long term. New fuels and technology based on the use of non-food feedstocks, lignocellulosic and waste streams in particular, are under development and will hopefully be commercialized in the near future. However, it is important to recognize that the technical challenges for the conversion of carbohydrates are significant, even with pure carbohydrates such as glucose.

Fractionation of lignocellulosics is well known and widely applied in the production of pulp and paper. The oldest processes known to efficiently obtain fermentable carbohydrates from lignocellulosic materials are the Giordani–Leone process with concentrated sulfuric acid [7], and the Rheinau–Bergius process (1931) with concentrated hydrochloric acid [8], both currently researched and applied by companies like BlueFire Ethanol, Green Sugar and HCl Cleantech; and the Organosolve (1971) [9], first applied in the Alcell process and currently researched by Lignol. However, techno-economic aspects have showed in the mid-1970s that these processes are not cost effective against producing carbohydrate streams from easily hydrolyzable starches such as from corn. New processes for lignocellulosic fractionation will have to be developed that can handle cheap feedstocks such as straw and other waste streams, but even then the nature of these feedstocks will remain challenging, as illustrated in Figure 1.7, and robust conversion processes need to be developed in parallel [10]. It is readily apparent that the sugar-containing



Simulated liquor from dilute-acid pretreated com stover

Actual liquor from dilute-acid pretreated com stover



–25% solids dilute-acid pretreated corm stover slurry (recently mixed drum)

–25% solids dilute-acid pretreated corm slurry (drum unmixed – 1 yr)

Figure 1.7 Photos of solutions derived from lignocellulosic biomass and pure carbohydrate, kindly supplied by Dr. E. Wolfrum of NREL, www.nrel.gov.

feedstocks will also contain biomass residues, tars, oligomers, inorganic metals from nutrient solutions, and sulfur, nitrogen and protein from fermentation-derived feedstocks. This mix of components will pose significant challenges in achieving high conversion, selectivity and long lifetimes of new catalytic systems or fermentative processes. Using unpurified hydrosylates/carbohydrate solutions derived from lignocellulosic feedstocks with minimal processing as feedstock will require even more catalyst and process development before implementation as the feedstock in a bio-refinery.

The most commonly used alcohol for blending with gasoline is ethanol. The production of ethanol from readily available carbohydrates is well known, especially in Brazil from sugar cane and in the USA from corn. Several other companies focus on the production of ethanol from lignocelluloses or from waste streams rich in carbohydrates, as discussed above. However, ethanol has many limitations, such as low energy density, hydrophilicity, corrosivity, miscibility/mixture stability, and cannot be transported in existing pipelines. Bio-butanol is an attractive alternative to ethanol with fewer implications. The benefits of butanol over ethanol as a fuel are shown in Table 1.4. Butanol offers better safety, improved fuel economy, can be blended with gasoline in high concentrations, and used without vehicle modifications. Another important advantage is that butanol can be transported in existing pipelines.

An overview of companies that are active in this field is shown in Table 1.5. Large companies like BP and DuPont are moving rapidly to introduce butanol.

Table 1.4 Representative properties of butanol versus ethanol and gasoline [11].

Property comparison	EtOH	BuOH	Gasoline
Energy content (BTU/gal)	78M	110M	115M
Reid V.P. @ 100°F (psi)	2.0	0.33	4.5
Motor octane	92	94	96
Air-to-fuel ratio	9	11	12–15

Table 1.5 Some companies actively involved in bio-butanol.

Company	Biofuel
Butamax (BP/DuPont)	iso-butanol n-butanol 2-butanol
Gevo	iso-butanol
Metabolic Explorer	n-butanol
Cobalt Biofuels	n-butanol
Green Biologics Ltd.	n-butanol
Tetravitae Bioscience	n-butanol (ABE)
Butalco	n-butanol

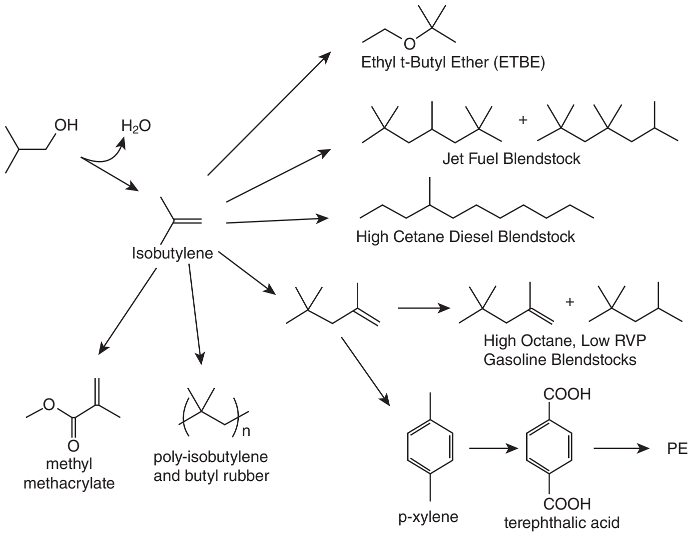
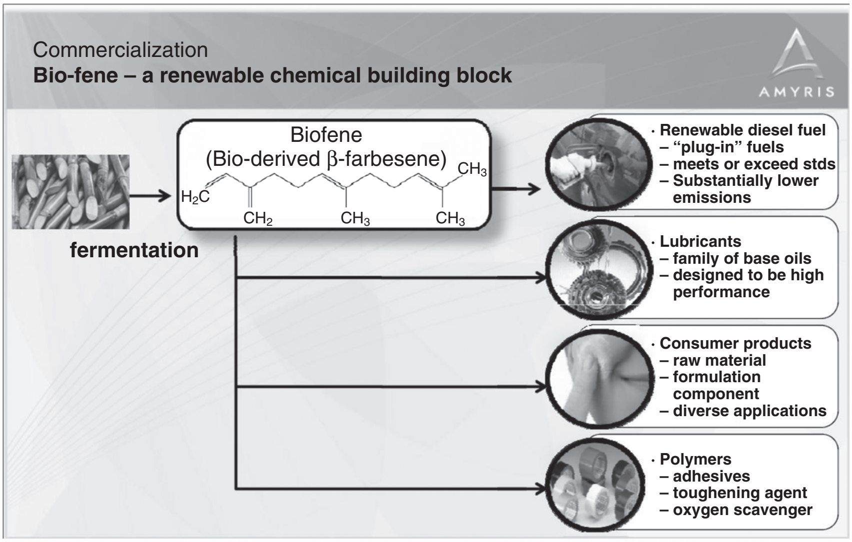


Figure 1.8 Some derivatives available from bio-isobutanol, adapted from Bernacki [12].

Smaller start-up companies, like Gevo and Cobalt Biofuels, have received significant venture capital funding and are making great progress with demonstrations in large pilot plants. Gevo Inc. was founded in 2005 and issued an IPO (initial public offering) in February 2011. At the start of the company, Gevo licensed intellectual property developed by Jim Liao at UCLA and Frances Arnold at Caltech. Gevo's fermentation processes can be retrofitted into existing ethanol plants with a limited amount of capital. The first of these retrofits was at St. Joseph, Missouri (2009) with an organism capable of making butanol. Of the three butanol isomers that their technology can produce, isobutanol is particularly attractive since it can be readily dehydrated to isobutylene, and offers an opportunity as a drop-in substitute as a renewable feedstock in existing processes, as shown in Figure 1.8. These cover a wide range of renewable chemicals and renewable fuels, such as jet fuel, high-octane gasoline, solvents, renewable terephthalic acid for PET bottles and butyl rubbers. In 2010 they announced a joint venture with Lanxess for the production of butenes, and in 2011 a collaboration with The Coca Cola Company on PET for beverage bottles [3].

Founded with technology developed at UC Berkeley and with initial venture capital funding another successful start-up is Amyris, Inc., which issued an IPO in September 2010. Their product platform is based on carbohydrate fermentation to the isoprene trimer, β-farnesene (Figure 1.9), which is insoluble in water and separates easily from the fermentation liquid [13]. After hydrogenation an attractive diesel fuel is obtained. However, the unsaturation in the β-farnesene also provides possibilities for a variety of monomers, polymers and specialty chemicals, in particular surfactant for use in soaps and shampoos, a cream used in lotions, a number of lubricants, and also the fully hydrogenated farnesane for solvent applications.



Commercialization

Bio-fene – a renewable chemical building block

AMYRIS

fermentation

Biofene (Bio-derived β-farbesene)

- **Renewable diesel fuel**
  - **“plug-in” fuels**
  - **meets or exceed stds**
  - **Substantially lower emissions**
- **Lubricants**
  - **family of base oils**
  - **designed to be high performance**
- **Consumer products**
  - **raw material**
  - **formulation component**
  - **diverse applications**
- **Polymers**
  - **adhesives**
  - **toughening agent**
  - **oxygen scavenger**

Figure 1.9 Family of products derived from Amyris Biofene, kindly supplied by Neil Reninger, CTO of Amyris, www.amyris.com.

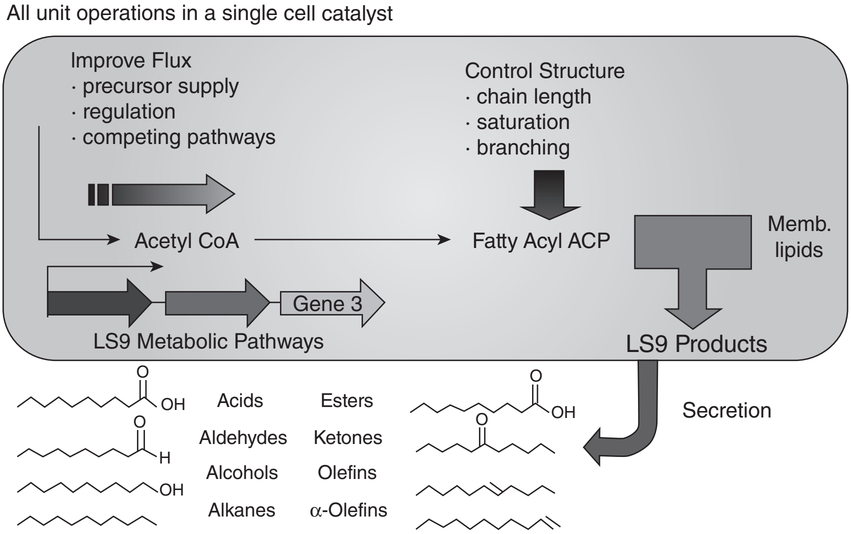
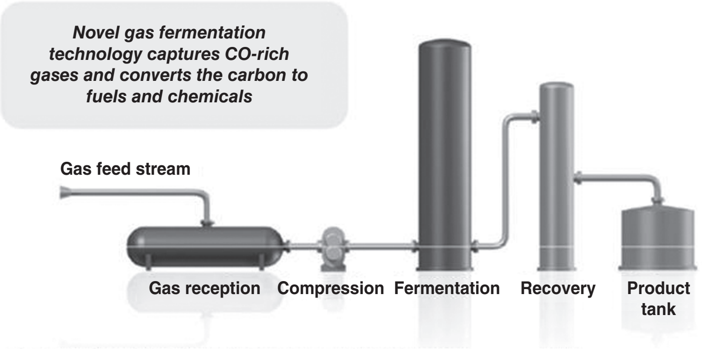


Figure 1.10 Potential biobased products produced by LS9, Inc., kindly supplied by S. del Cardayre, VP R&R from LS9, www.ls9.com.

Another bio-company, which converts carbohydrate to hydrocarbon products that readily separate from the fermentation broth, is LS9 Inc. founded in 2005. They have developed biology for the fermentation of carbohydrates to linear hydrocarbons, as shown in Figure 1.10. Organisms that naturally produces lipids have been genetically altered such that they are able make a variety of linear hydrocarbons.



- **Innovative:** Microbe uses gases as its sole source of energy
- **Proprietary:** LanzaTech has filed 58 patents, including two proprietary microbe patents
- **Not just about ethanol**
- **Integrative:** Direct production of fuels and chemicals (2,3 Butanediol, Isoprene, Propanol, Butanol, MEK); multi step production of chemicals and chemical intermediates (olefins)
- **Thermo Chemical Opportunities:** 2,3 Butanediol produced through the LanzaTech Process can be used to make true “Drop in” hydrocarbin fuels (gasoline, diesel, jet fuel).

Figure 1.11 The LanzaTech process for converting CO-rich streams to ethanol and 2,3-butanediol, kindly supplied by S. Simpsoon, CSO and co-founder of LanzaTech, www.lanzatech.co.nz.

Further modifications to the organism can yield an even wider array of products, including alcohols, olefins, ketones and aldehydes.

Though ethanol and other alcohols can readily be obtained by fermentation, it has been restricted to the use of sugar feedstocks, be it sugar cane, corn or lignocellulose. An alternative is being commercialized by LanzaTech Inc., a start-up company founded in 2005 in New Zealand. LanzaTech’s commercial plants will effectively convert a variety of non-food, low-value gas feedstocks into bioethanol and other platform chemicals. They have developed a proprietary technology that allows fermentation of CO-rich streams into ethanol and other products like 2,3-butanediol. They have been operating a pilot plant at a steel mill in New Zealand and have just announced construction of a 100 000 gallon per year demo plant in collaboration with Bao Steel in China. Following a successful scale-up of their demo facility, commercial plants are planned for China, South Korea and India. Although, initially using CO-rich gases, a by-product from steel manufacturing, it is easy to envisage that their process can be coupled to bio-mass gasification and thus use non-carbohydrate sources as well (Figure 1.11).

The future of biofuels will, however, be beyond ethanol, butanol and FAME-based biodiesel. Next generation fuels will be hydrocarbon fuels from non-food, lignocellulosic feedstocks. Several options are under investigation, but key in all of these is the removal of the abundant oxygen present in the biomass molecules, especially carbohydrates.

Biomass gasification potentially provides an excellent method of converting lignocellulosic feedstock into synthesis gas. The production of syngas is technically feasible but presents a number of challenges to remove tars and inorganics, which are severe poisons to downstream Fischer–Tropsch or higher alcohol synthesis catalysts [14]. An excellent overview of potential processes to convert lignocellulosic feedstocks to advanced biofuels can be found in a report from a DOE workshop in 2007 [15]. New gasifiers are under development around the world since the variable composition of biomass is significantly different from natural gas or coal, the traditional sources of syngas. An early pioneer in the field was Range Fuels, which built a demo plant in Georgia to gasify wood chips to syngas followed by an alcohol synthesis primarily to methanol and ethanol. Unfortunately, the plant did not work as expected and was closed [16]. Currently, Ineos New Plant Bioenergy, LLC (a division of Ineos Chemical Company) is constructing a commercial demonstration facility in Indian River County, Florida to ferment synthesis gas derived from lignocellulosic feedstocks into ethanol. Hence, a large-scale operation to validate the potential for this thermochemical and biological route should be demonstrated [17].

One concept under consideration by many companies is field densification, or partial dehydration of lignocellulosic materials. A preferred process, called flash pyrolysis, involves heating the biomass very quickly (~$100\,°\mathrm{C\,s^{-1}}$) to a temperature of about 400 °C [18]. During this heating step, volatile gases are produced, along with a solid char (from the lignin) and a wet oil called pyrolysis oil. In general, the char and the volatile gases that are co-produced are burned to provide the heat needed for the process. The oil tends to be very acidic and corrosive, highly colored, immiscible with hydrocarbon fuels, and contains about 20–30% residual water. It is also relatively unstable and its composition changes with time. Stabilizing and upgrading of the pyrolysis oil prior to shipment is one of the many challenges to commercial use. The pyrolysis treatment will significantly deoxygenate the pyrolysis oil. UOP and Ensyn have formed a joint venture (JV) called Envergent Inc. with the purpose of developing technology to hydrogenate the pyrolysis oil obtained by the RPT (rapid thermal processing) process of Ensyn to a useful hydrocarbon fuel. In their current process woody biomass is brought in contact with the hot sand at about 510 °C for 2 s to produce pyrolysis oil (Figure 1.12). Dynamotive is another fast pyrolysis company that has several commercial plants making pyrolysis oil for energy use and is developing a two-stage hydrogenation process that first stabilizes the oil by reducing water and oxygen content and subsequently the first product to give a gasoline/diesel fuel.

An alternative approach in pyrolysis is pursued by KiOR Inc. [19], by using a catalyst during the pyrolysis step. The effect is very significant since the catalyst allows the pyrolysis of the biomass at a lower temperature and at the same time reduces the oxygen content of the pyrolysis oil. Their biomass catalytic cracking process (BCC) produces a less-acidic oil that separates from the aqueous phase and can be readily processed to produce fuels (Figure 1.13).

Other companies are actively investigating the option of chemo-catalytic routes to convert carbohydrate-rich streams to fuel intermediates. In general, the strategy

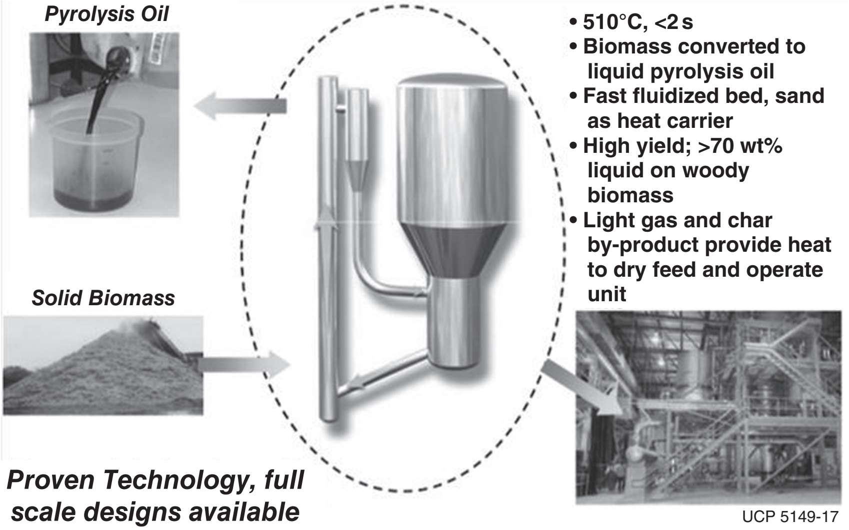


Figure 1.12 Honeywell/UOP's Invergent's process for production of pyrolysis oil, kindly supplied by J. Holmgren, formerly Honeywell UOP, www.uop.com.

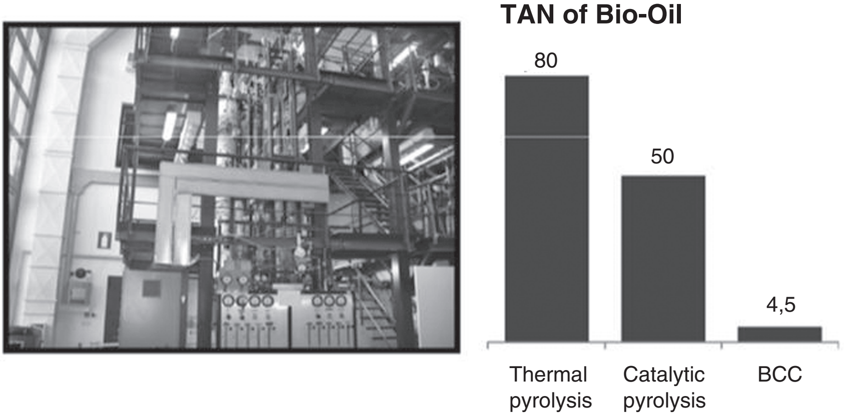
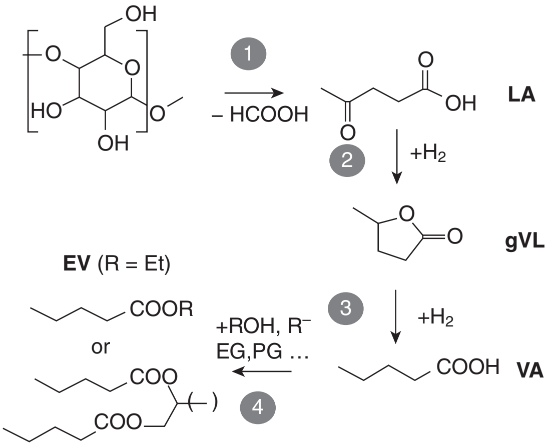


Figure 1.13 Total acid numbers for pyrolysis oils from KiOR's catalytic pyrolysis technology (BCC), kindly supplied by P. O'Conner, founder of KiOR, www.kior.com.

chosen here is to leave the carbon backbone of the carbohydrate molecule intact, and remove the oxygen atoms, either by dehydration, decarbonylation/decarboxylation or by hydrogenation. The dehydration route is the most preferred as it is not accompanied by loss of carbon (decarbonylation/decarboxylation) or usage of hydrogen (hydrogenation).

Dehydration of carbohydrates leads to furfural from C5 carbohydrates and hydroxymethyl furfural (HMF) from C6 carbohydrates. The latter rapidly reacts further to give levulinates. Both furfural, HMF and levulinates can serve as the starting point for a new class of biofuels. Currently no commercial process is known for HMF, but levulinates are produced by Biofine Renewables, LLC, directly from biomass (see more details in Section 1.4). Several groups in academia are working on related processes with HMF, such as the dimethylfuran or nanones from the Dumesic group [20] and the methyl furans (RWTH-TMFB). Industrially, Avantium and Shell, both from the Netherlands, have claimed biofuels via furfural, HMF and Levulinate pathways. A group at the University of Maine has conducted work in the production of higher alcohols liquid biofuel via acidogenic digestion and chemical upgrading of industrial biomass streams. The resulting fuels have a very low acid number [21].

Shell International has claimed the use of tetrahydrofurfuryl ethers derived from hydrogenation and etherification of furfural [22]. More recently, their focus has shifted to valeric acid based fuels (see Figure 1.14) still using levulinate as the starting point [23]. The levulinates are typically obtained from C6 carbohydrates, via HMF as the intermediate, a process currently being developed by BioFine, or from C5 via furfural by the process developed by the Quaker Oats Company in 1922. Shell has claimed routes from furfural by hydrogenation to furfuryl alcohol followed by a rearrangement to levulinate. The possibility to use both C5 and C6



	1. Hydrolysis	2. Hydrogenation	3. Hydrogenation	4. Esterification
Catalyst	H_2SO_4	Pt/TiO_2	Pt/ZSM-5	IER
Selectivity	50–60%	>95%	>90%	>95%
Productivity	$>0.1\,h^{-1}$	$>10\,h^{-1}$	$>1\,h^{-1}$	$>0.02\,h^{-1}$
Concentration	<5%	>90%	>50%	>50%

Figure 1.14 GVL-based fuels [23]. LA = levulinic acid, gVL = gamma-valerolactone, VA = valeric acid and EV = ethyl valerate.

carbohydrates fits very nicely with the potential to use non-food lignocellulosic feedstocks for these fuels.

In the process described by Avantium Chemicals, carbohydrates are dehydrated in alcoholic solutions to give the stable ethers of hydroxymethyl furfural and furfural. Further processing yields ethers of furfuryl alcohol and bishydroxymethylfuran and the corresponding tetrahydro equivalents. Depending on the type of alcohol used the ethers and bis-ethers can be applied as gasoline or as diesel [24].

It remains clear that a large source of biomass will be needed to make a significant contribution to society's need for transportation fuels. A 2005 report from the USDA, updated in 2012 [25], suggested that the US had about 1.366 billion tons of agricultural and forest residue available but that this amount of biomass would satisfy only about 30% of the US transportation fuel needs. An issue that holds merit for most biomass sources is that it has a high water content. Economical transportation over long distances is usually considered uneconomical and it is estimated that conversion units will need to be located within about 50 to 80 miles or less, depending on the type of biomass. Much of the biomass available is located at significant distances from any potential biorefinery and end-users, thus requiring small-scale conversion to condensed, water-free intermediates before it may be economically transported.

1.4
Renewable Chemicals

Several companies focus on chemicals derived from biomass, even more than for fuels, for which other clean energy sources and uses can be envisaged, such as electric cars via solar panels. The production of renewable chemicals inherently requires carbon atoms from the biomass. Several companies are working on biological, catalytic or thermochemical routes to chemicals as they generally have a higher value than fuels. In some cases the products are direct drop-in replacements, while other companies obtain new chemicals and products. An important and commonly cited report was prepared by PNNL and NREL [6], which will be discussed in detail in Chapter 3. They proposed 12 molecules (see Table 1.6) that

Table 1.6 The top carbohydrate-derived building blocks outlined by DOE [6].

Top 12 carbohydrate-derived building blocks	
Succinic, fumaric and maleic	Itaconic acid
2,5-Furan dicarboxylic acid	Levulinic acid
3-Hydroxyl propionic acid	3-Hydroxybutyrolactone
Aspartic acid	Glycerol
Glucaric acid	Sorbitol
Glutamic acid	Xylitol/arabinitol

would be attractive building blocks for future renewable chemicals. This report has stimulated a very significant amount of research within the academic and industrial communities.

Several of these building blocks can be made via fermentative or enzymatic routes and are thus outside the scope of this book. Nevertheless, as was already concluded in earlier sections, the role of fermentation in bio-mass conversion will certainly be an important technology in future bio-refineries. Genencor and Rivertop describe enzymatic and thermochemical processes for the carbohydrate acids, gluconic and glucaric acids [26, 27]. Likewise, for the amino acids aspartic and glutamic acids, which are produced largely in China by a variety of companies, the Fufeng group being the largest.

The chemical synthesis and production of some of these building blocks are already well known. In the mid-1950s Roquette in France developed processes for sorbitol and xylitol. These processes are based on the hydrolysis of starches to glucose and subsequent selective hydrogenation to sorbitol and can be modified to give other polyols, that is, maltitol, mannitol, xylitol and arabinitol. The sorbitol is then further converted into the anhydride isosorbide, which is considered a potential diol building block for renewable polyesters [28].

One molecule that is receiving considerable attention is succinic acid. A number of small and large companies (BioAmber, Myriant, DSM, BASF, and others) have announced plans to commercialize biobased succinic acid by fermentation and its derivatives by chemical conversion. The world's first commercial demo-plant of succinic acid was started in France in January 2010 by BioAmber Inc. with nominal capacity of $220\,\mathrm{t\,a^{-1}}$, with new full-scale plants being planned in Canada and Thailand. The petrochemical route for producing succinic acid is by hydrogenation of maleic acid, obtained via butane oxidation. A biobased source of succinic acid and its derivatives would be drop-in replacements for the petroleum-derived compound and could even be used to supply bio-maleic acid and maleic acid anhydride by selective oxidation. The markets for products derived from biobased succinic acid (polymers, plastics, solvents, adhesives, and coatings) (Figure 1.15) are significant. So it is not surprising that it has attracted the attention of so many companies.

First described in 1875 by Freiherrn, Grote and Tollens [30], levulinic acid has been of interest for many years as a bifunctional keto-acid but it has never been made on a commercial scale [31]. Biofine Renewables, LLC has developed a thermochemical process that produces levulinic acid, furfural, formic acid and char from a wide variety of carbohydrate-containing biomass feedstocks. The process uses two reactors: in the first the biomass is broken down into small components, such as carbohydrates and hydroxymethylfurfural, which are then further converted in the second reactor to levulinic acid. The conditions employed are extreme, with high temperatures and pressures in the presence of acid catalyst, yielding about 50% levulinic acid. With the ketone and acid group functionality, levulinic acid can be converted to a wide variety of compounds. Currently three demo-plants are operational, the largest in Caserta, Italy with a $50\,\mathrm{t\,d^{-1}}$ lignocellulosic feed intake. A study by Hayes [32] suggests that the production of ethyl levulinate can

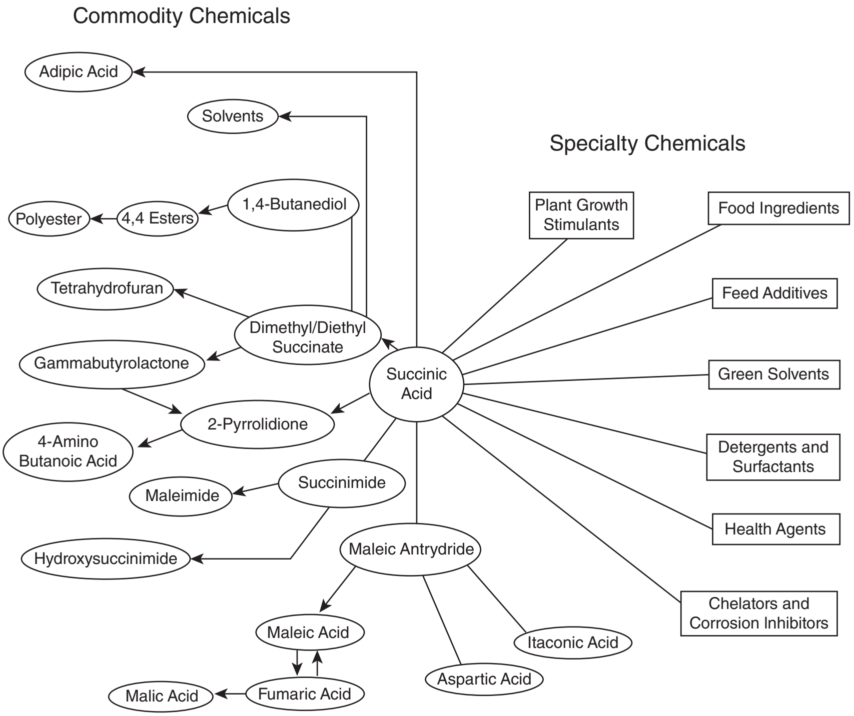


Figure 1.15 Succinic acid as a biorenewable platform chemical [29].

be competitive at a 400 kt a^{-1} scale, if all energy required is generated on-site from waste streams.

DuPont has disclosed a diverse portfolio of products that can be obtained such as *N*-alkylpyrrolidones, monomers for the preparation of thermally stable polymers, ionic liquids and nylon intermediates (Figure 1.16) [31]. While many of these materials are exciting new renewable-based chemicals, none have reached commercial production yet, due to the absence of a high volume levulinic acid production process at sufficiently low cost.

Segetis Inc., a Minnesota-based venture capital backed company, also uses levulinic acid as the basis of their product portfolio [33]. They developed a novel class of ketals formed by the reaction of diols and polyols with the ketone group of levulinic acid. In particular, by using glycerol and levulinic acid, both part of the DOE “Top 12” list (Table 1.6), new ketal products are produced which have excellent functionality and can potentially replace existing petroleum-based solvents, surfactants and plasticizers (Figure 1.17).

Furandicarboxylic acid (FDCA) is another of the DOE Top 12 molecules, and has potential to replace terephthalic acid [34]. It has been shown that this could be prepared by oxidation of hydroxymethylfurfural, HMF. Production of HMF has long been researched, but even with two pilot plants having been commissioned no commercial process has been established that can produce HMF at low cost

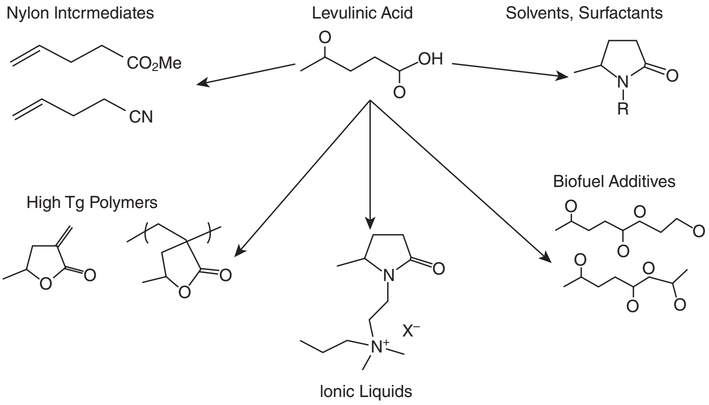
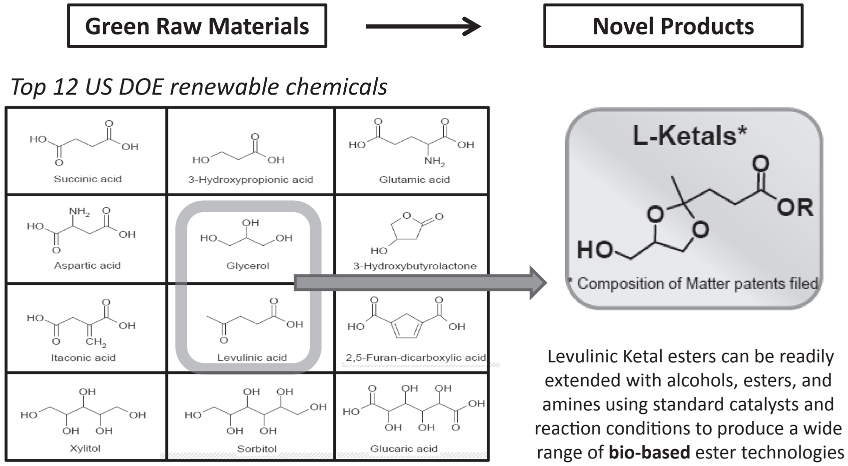


Figure 1.16 Selected derivatives of levulinic acid, adapted from Ritter [31].



Levulinic Ketal esters can be readily extended with alcohols, esters, and amines using standard catalysts and reaction conditions to produce a wide range of **bio-based** ester technologies

Figure 1.17 Segetis ketals are derived from diols and levulinic acid.

[35]. Avantium is pursuing the use of HMF-ethers as renewable platform chemicals (Figure 1.18) [24] and has recently announced the start-up of a pilot-plant in the Netherlands. An advantage of forming the HMF-ether is that it is much more stable and easier to work with than HMF. Having shown that the HMF-ethers can easily be oxidized to FDCA, polymers of FDCA have now been made. Especially, the FDCA polyesters (PEF) are potential replacements for terephthalic acid esters. The new PEF polymer had a reported glass transition temperature, $Tg = 86\,°C$ versus PET with $Tg = 81\,°C$, whereas the gas barrier properties for CO_2 and O_2 are at least 2 and 9 times better, respectively, compared to PET, allowing it to be used in demanding applications such as bottles and food packaging [24]. The main price drivers for biobased FDCA are the feedstock price and economy of scale. However, at a $>300\,kT\,a^{-1}$ scale the price of FDCA will be <€1000 per ton, and therefore competitive with pTA produced on the same scale.

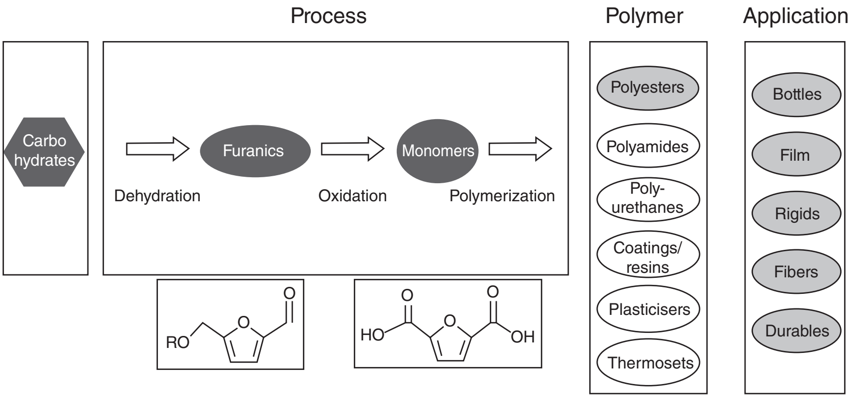


Figure 1.18 The Avantium process for producing furanic polyesters [36].

1.5
Conclusions

The intent of this chapter was to provide examples of the creativity and innovation being developed in the field of bio-renewable fuels and chemicals. Today new start-up companies mostly lead the effort. These companies are playing a key role in the development of renewable fuels and chemicals. Not all will be successful, larger oil and chemical companies will acquire some, and some will grow into new companies. With luck, perseverance, and significant funding, a significant portion of the world's needs for fuels and chemicals will someday be based on renewable feedstock.

In the rest of this book, it will be shown that chemical catalytic processes, in combination with fermentative processes, will play a pivotal role in creating cost-effective and sustainable production methods.

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