Review



Review of US and EU initiatives toward development, demonstration, and commercialization of lignocellulosic biofuels

Venkatesh Balan, Michigan State University, Lansing, MI, USA David Chiaramonti, University of Florence, Italy Sandeep Kumar, Old Dominion University, Norfolk, VA, USA

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Abstract: Advanced biofuels produced from lignocellulosic biomass offer an exciting opportunity to produce renewable liquid transportation fuels, biochemicals, and electricity from locally available agriculture and forest residues. The growing interest in biofuels from lignocellulosic feedstock in the United States (US) and the European Union (EU) can provide a path forward toward replacing petroleum-based fuels with sustainable biofuels which have the potential to lower greenhouse gas (GHG) emissions. The selection of biomass conversion technologies along with feedstock development plays a crucial role in the commercialization of next-generation biofuels. There has been synergy and, even with similar basic process routes, diversity in the conversion technologies chosen for commercialization in the EU and the US. The conversion technologies for lignocellulosic biomass to advanced biofuels can be broadly classified in three major categories: biochemical, thermochemical, and hybrid conversions. The objective of this review is to discuss the US and EU biofuel initiatives, feedstock availability, and the state-of-art conversion technologies that are potentially ready or are already being deployed for large-scale applications. The review covers and compares the developments in these areas in the EU and the USA and provides a comprehensive list of the most relevant ongoing development, demonstration, and commercialization activities in various companies, along with the different processing strategies adopted by these projects. © 2013 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: biofuels; thermochemical; biochemical; commercialization; lignocellulosic biomass

Introduction

fforts are underway to transform the petroleum-based economy to a bio-based economy. As the name implies, a bio-based economy is focused

on deriving fuels and chemicals from renewable plant-, algal-, or microbial-based materials such as lignocellulosic biomass. The development of new processes for fuels and chemicals from lignocellulosic feedstocks represents an extremely important field for R&D and



industrial innovation within the bioenergy sector today. While the fundamental and applied research for technology development is carried out in research institutions, companies are using those technologies to actively scale up to demonstration- and commercial-scale activities. In general, major motivations to launch second-generation technologies into full-scale commercial applications will increase the sustainability of biofuel production (compared to first-generation biofuels that are produced from food-grade materials). At the same time, venture capital and government funds are available and have been used by innovative companies working on biotech, biochemical, and thermochemical processes to demonstrate that the processes are reasonable at a large scale. Several companies around the world are currently setting up state-of-the-art technologies that produce advanced biofuels from lignocellulosic biomass. Among them, companies in United States (US) and the European Union (EU) are actively involved, since the basic policy framework for producing biofuels and biochemicals is favorable in these regions.

A definition for the term 'advanced biofuels' is not yet clearly agreed. In the Renewable Fuels Standard of 2010, advanced biofuels were defined as 'non-grain' based fuels³ (other than corn-based biofuels). In 2011, International Energy Agency (IEA) gave the following definition for advanced biofuel technologies: 4 'Conversion technologies which are still in the research and development (R&D), pilot or demonstration phase, commonly referred to as second- or third-generation. This category includes hydro treated vegetable oil (HVO), which is based on animal fat and plant oil, as well as biofuels based on lignocellulosic biomass, such as cellulosic-ethanol, biomass-to-liquids (BtL)-diesel and bio-synthetic gas (bio-SG). The category also includes novel technologies that are mainly in the R&D and pilot stage, such as algae-based biofuels and the conversion of sugar into diesel-type biofuels using biological or chemical catalysts.' Thus, the focus is more on the technology rather than on selecting the feedstock.

The definition of advanced biofuels in the European context is instead still under discussion. The European Commission (EC), for instance, in its recent proposal of revision of the Renewable Energy Directive (RED),⁵ defined advanced biofuels⁶ as biofuels that 'provide high greenhouse gas savings with low risk of causing indirect land use change (ILUC) and do not compete directly for agricultural land for the food and feed markets'. Recently, the leaders of Sustainable Biofuels Group, the group merging the major EU industries working exclusively on second-generation biofuels, proposed the following definition⁷: '(1) produced from lignocellulosic feedstocks

(i.e. straw, bagasse, empty fruit bunch, forestry residues, lignocellulosic energy crops, crude tall oil & tall oil pitch), non-food crops (i.e. grasses, miscanthus, algae), or industrial waste and residue streams or manufactured from the biomass fraction of municipal wastes, (2) having low CO₂ emission or high GHG reduction, and (3) reaching zero or low ILUC impact.'

The key element in the debate on defining advanced biofuels remains their sustainability and their conflict with food crops. In our opinion, advanced biofuels are any fuels that use advanced technologies to deal with lignocellulosic materials or other unconventional feedstocks that are cultivated on marginal land or that use agricultural/forestry residues. The efficient integration of energy flows in the process makes the overall greenhouse gas emissions and environmental balance of advanced biofuels very favorable and largely superior to most of the so-called first-generation biofuels (excluding the sugarcane-to-ethanol case).

Following the Energy Independence and Security Act of 2007, 8 the US set a target of 36 million gallons per year (MGPY) advanced biofuels by 2022,9 thus forecasting that non-grain-based biofuels (according to the RFS reported above, this includes sugarcane ethanol, lignocellulosic and algal biofuels, etc., but excludes cornstarch-based fuels,) will enter the marketplace at a higher volume. In February 2012, the US Department of Energy (DOE) invested more than US\$1 billion in 29 integrated biorefinery projects to produce advanced biofuels, including ethanol, butanol, gasoline, diesel, and jet fuels; chemicals; and power. Out of the 29 projects, the DOE supported 16 cellulosic ethanol projects with US\$766 million support, 11 hydrocarbon fuel projects with US\$326 million support, 1 butanol project with US\$30 million support, and one succinic acid production facility with US\$50 million support. Among these projects there were two R&D bench-scale demonstration facilities, 12 pilot-scale demonstration facilities, 9 full-scale demonstration plants, and 6 commercial scale plants.

Also in 2007, the EU set its 20-20-20 targets, referring to the goals of increasing the share of renewable energy to 20% (with 10% contribution of renewable alternatives in transportation fuels), improving energy efficiency by 20%, and reducing greenhouse gas (GHG) emissions by 20%, all by 2020, as well as a number of other policies that were also developed and put in place. Among these policies, sustainability criteria where set for biofuels in the Renewable Energy Directive (RED), which mainly address minimum GHG saving requirements, and protection of land with high biodiversity or carbon stock.

More recently, the EC issued a proposal for amending 'the directive 98/70/EC' and 'the directive 2009/28/EC'.⁶ This proposed revised directive, also known as the ILUC directive, better specifies the conditions and the targets for biofuel production in the EU under the light of ILUC considerations. The key issues in the Commission's proposal are the following: (i) 5% limit to the amount of first-generation biofuels that can count toward the RED targets, (ii) enhanced incentives for advanced non-land using biofuels (quadruple accounting), (iii) increase to 60% GHG savings requirement for new installations, and (iv) ILUC factors included in the reporting of GHG savings in both directives.

In addition, an explicit list of feedstocks counting between two and four times is given in Annex IX of the document. The consultation with the European Parliament, the council member states and the stakeholders is ongoing, and a decision will be reached soon. The discussion about the future policy framework in the EU (beyond 2020) has also started, with the very recent Green Paper by the EC. Here the EC calls for another consultation (open until 2nd July 2013) focused on addressing targets, the coherence of policy instruments, the competitiveness of the EU economy, and the different capacity of the member states.

The major EC programs¹¹ supporting the development of R&D and demonstration in the field of biofuels are the 7th Framework Program (7FP), the European Industrial Bioenergy Initiative (EIBI) (which addresses only large-scale industry-led projects), and the Intelligent Energy Program (not supporting concrete implementation, but market, barrier removal, information and dissemination actions).

In regards to lignocellulosic ethanol production programs, the EC supported 7 industrial demonstration projects through the 7FP for a total of more than €70 million. Recently (December 2012), the EC awarded over €1.2 billion to 23 highly innovative renewable energy demonstration projects under the first call for proposals for the NER300 funding program. Among these, a considerable amount of resources (~€630 million) was allocated to advanced biofuels, with ~€82 million for biochemical routes and the rest (~€548 million) for thermochemical.

With respect to projected production costs of lignocellulosic ethanol, recent communications by major EU industries involved in the construction or operation of industrial demo plant seems to converge around a cashcost target of 1.5–2 US\$/gal.^{12,13} This cost estimate is very competitive with projected costs for other advanced biofuels production chains, as estimated by the DOE.¹⁴ On the other hand, the cost of biodiesel from algae were instead estimated at 10.66–19.89 US\$/gal, (one order of magnitude higher than the options previously reported).

It is widely believed that the biofuel process cost will come down as the biorefining technology matures, as it has always happened in the past for new technologies entering the market. A good example is Brazil, where the cost of sugarcane ethanol was substantially reduced mainly due to (i) learning effect, (ii) large-scale operations, and (iii) efficient system integration (including the whole of the supply chain): this was well represented by the well known 'Goldemberg curve', that reported the reduction of ethanol costs in Brazil during the years. In the case of highly innovative technologies, it is reasonable to expect a significant learning factor, which will drive downwards the production costs quite rapidly compared to more mature/less innovative solutions.

Commercial R&D and scale-up activities in the US and EU

The assessment of most relevant EU and US initiatives in the field of lignocellulosic fuels was carried out though the analysis of R&D projects, literature, ¹⁵ data sources, ^{16–18} other similar work, ¹⁹ company websites and personal contacts with several of the companies listed in Tables 1 and 2.

US projects

In the US, the National Advanced Biofuels Consortium (NABC) is a major research initiative and partnership of 17 industry, national laboratory, and university members. The goal of the NABC is the development of technologies to convert lignocellulosic biomass feedstocks to advanced biofuels. Led by the National Renewable Energy Laboratory (NREL) and Pacific Northwest National Laboratory (PNNL) and supported with US\$35 million of American Recovery and Reinvestment Act (ARRA) funding from the DOE and US\$14.5 million of partner funds, NABC is investigating six process strategies including (i) fermentation of lignocellulosic sugars, (ii) catalysis of lignocellulosic sugars, (iii) catalytic fast pyrolysis, (iv) hydrothermal pyrolysis, (v) hydrothermal liquefaction, and (vi) syngas to distillates for converting lignocellulosic biomass feedstock to advanced biofuels.

At the industrial level, 31 US projects are currently involved with the development of advanced biofuels from lignocellulosic biomass (Table 1). With respect to the different biomass conversion routes shown in Fig. 1, 17

Table 1. Biofu	iels commercia	Table 1. Biofuels commercialization activities in the U	s in the US.				
Company <i>Proj/Acron.</i>	US Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
				Thermochemical			
British Airways and Solena	Solena Headquarter: Washington DC, USA	Demo (Thermochemical)	Bio-SPK (Synthetic Paraffinic Kerosene) Synthetic Diesel (road or marine MGO) Naphta	 60.6 ML/y (16 MGPY jet fuel) 40 MW power 	Waste-biomass	Soon break ground, opera- tional in 2015 as Solena GreenSky London project in East London, EU	Solena Integrated Biomass Gasification to Liquid ("IBGTL") Biomass gasification + Cleaning + FT reactors + FT fuels upgrading www.solenafuels.com
Cool Planet BioFuels	Camarillo, CA	Pilot (Thermochemical)	Liquid hydrocarbon fuels Biochar	n.a	Wood chips, agri- cultural waste	Planning several commercial plants	Proprietary two-step thermal/ mechanical processor which pro- duces multiple distinct gas streams for catalytic upgrading to liquid fuels. http://www.coolplanetbiofuels.com/
Enerkem	Westbury, Quebec (Canada) Edmonton, Alberta (Canada) Varennes, Québec (Canada) Pontotoc, MS	Demo (Thermochemical)	Bioethanol, biomethanol, Syngas, acetates	• Commercial 37.85 ML/d (10 MGPY)	Sorted municipal solid waste and wood residues	Construction	Canada based company with proprietary technology focus on syngas to ethanol/chemicals via catalysis route http://www.enerkem.com/en/home.html
Ensyn Corporation	Belridge, CA	Demo (Thermochemical)	Renewable liquid fuels and chemicals	• 120,000 L/day (1000 barrels/day) renewable heavy oil	Wood residues and celloulosic wastes	Commercial Demonstration Facility commis- sioned in 2004	Rapid thermal processing process, Ensyn and UOP, a Honeywell company, joined forces with the creation of Envergent Technologies LLC. http://www.ensyn.com/
Honeywell/ UOP/Envergent	Kapolei, Hawaii	Demo (Thermochemical)	Green Jet Fuel	n.a	Forestry and agri- cultural residuals	Demo is expected to start up in 2014. 50 M gallons of drop-in green transportation fuels per year is planned at same location	Fast pyrolysis and catalytic upgradation process (Envergent Technologies RTP TM process), world-wide technology provider, developed UOP/Eni Ecofining TM process to produce Honeywell Green Diesel TM and Green Jet Fuel http://www.envergenttech.com/http://www.uop.com/
Kior Inc.	Pasadena, TX (Pilot) Columbus, MS (Commercial)	Demo (Thermochemical)	Green gasoline Green diesel Fuel 0il	• Commercial 41.64 ML/y (11 MGPY)	Woody biomass	Started commercial operation in Nov. 2012	Fluid catalytic cracking, additional commercial plants con- struction are planned in MS of 151.4 ML/y (40 MGY) capacity from 2013 http://www.kior.com/

Renmatix	Kennesaw, GA, (Pilot) King of Prussia, PA, (demo)	Pilot (Thermochemical)	Cellulosic sugars	100 kg/d (220 lb/d) woods to sugar at pilot	Woody biomass	Demonstration plant 3 t/d bio-mass processing is under construction in PA.	Supercritical water hydrolysis, aimed to produce cellulosic sugar at this stage http://renmatix.com/
Rentech, Inc.	Commerce City, CO	Pilot (Thermochemical)	Syngas and ultra- clean synthetic fuels	0.568 ML/y (0.15 MPGY) synthetic fuels	Wide range of cel- lulosic biomass feedstocks	Product demonstration (PDU) unit is in operation since 2008	Owns the Rentech-SilvaGas and the Rentech-ClearFuels biomass gasification technologies http://www.rentechinc.com/
Virent	Madison, Wisconsin	Demo (Thermochemical)	Mixtures of "drop-in" hydrocarbons (gaso- line, diesel, jet fuels, and chemicals)	0.038 ML/y (0.01MGPY) Biogasoline	Mixed cellulosic feedstocks - corn stover and pine harvest forest residuals	Commercialization is not planned yet	Aqueous phase reforming , catalytic upgradation of sugar to liquid fuels http://www.virent.com/
				Biochemical			
Abengoa Bioenergy	i. York, NE ii. Hugoton KS,	Pilot (Biochemical) Commercial (Biochemical)	Bioethanol	0.076 ML/y (0.02 MGPY) 95 ML/y EtOH (25 MGPY) and 18 MWe electricity	330 t/y corn stover 350,000 t/y (mix- ture of agricultural waste, non-feed energy crops and wood waste)	Pilot in operation since Sep. 2007 Commercial under construction (exp. end 2013-early 2014)	Dilute acid pre-treatment and first-of-its-kind commercial-scale enzymatic hydrolysis conversion of lignocellulosic biomass, Over 26,000 h of pilot operation www.abengoabioenergy.com/web/en
Amyris	Emeryville, CA	Pilot (Biochemical)	Renewable diesel Renewable Jet Fuel	n.a	Sugarcane	Commercial operation in Brazil by early 2013	Commercial location in Brazil Synthetic biology platform to pro- duce Biofene ®. Biofene, Amyris's brand of a long- chain, branched hydrocarbon molecule called farnesene (trans-8- farnesene). Proprietary yeast strains http://www.amyris.com/
BIOGASOL	USA - Boardman, Oregon	Demo (Biochemical)	Bioethanol, Hydrogen, Methane, Lignin- rich stream	• 10 ML/y EtOH (2.64 MGPY)	5.8 t/h Straw, hybrid pop- lar, corn stover	Cancelled	Proprietary MaxiSplit process based on Pre-treatment - Carbofrac TM and C5 Fermentation - Pentoferm TM . www.biogasol.com
BlueFire Renewables	Anaheim, CA (pilot) Lancaster, CA and Fulton, MS (commercial)	Pilot/Demo (Biochemical)	Cellulosic Sugars Bioethanol Gypsum, Lignin, and protein cream	Pilot 0.091 t/d (200 lb/d) cellulosic sugars Commercial- 14.76 ML/y (3.9 MGPY) bioethanol at Lancaster, CA Commercial-71.92 ML/y (19 MGPY) bioethanol at Fulton, MS	Mixed feedstock (wood, paper waste, bagasse, forest residue)	Pilot in operation since 2003, Commercial from 2014	Concentrated acid hydrolysis process to hydrolyze carbohydrates and fermentation. http://bfreinc.com/

Table 1. (Continued)	tinued)						
Company Proj/Acron.	US Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
Blue Sugars	Rapid City, SD (Pilot) Upton, WY (Demo)	Pilot/Demo (Biochemical)	Bioethanol	• 1.0 – 2.0 dry tons / hour various types of lignocellulosic biomass	Cellulosic biomass	Develops bioetha- nol process technologies	Thermo-mechanical pretreatment and enzymatic hydrolysis process, commercial plant planned in Brazil. Globally the first company to record cellulosic ethanol renewable identification numbers (RIN) credits issued by the EPA.
Butamax [™] Advanced Biofuels LLC.	Wilmington, De	Demonstration plant in UK (Biochemical)	Biobutanol	n.a	Different types of lignocellulosic feedstocks	The technology demonstration plant will use all the lignocellulosic feedstocks currently used for bioethanol production.	A joint venture created by BP and DuPont. Constructing a biobutanol technology demonstration plant in Hull, UK expected to be operational by 2013. Butamax has patents and patent applications covering recombinant microorganisms optimized as well as manufacturing processes. http://www.butamax.com/
BP Biofuels	Jennings, Louisiana	Demo (Biochemical)	Bioethanol	• 5.9 ML/y (1.4 MGPY) bioethanol	Lignocellulosic biomass	Acquired Verenium's cel- Iulosic biofuels business	BP Biofuels Global Technology Center is a purpose-built R&D facil- ity in San Diego, California and also operates 1.4 MGPY cellulosic dem- onstration facilities in Jennings, LA. Cancelled its pursuit of commercial- scale cellulosic ethanol production in the USA in Oct 2012.
Chemtex/Beta Renewables (Project Alpha)	Clinton, NC	Commercial (Biochemical)	Bioethanol, Lignin	• 75.7 ML/y (20 MGPY)	Dedicated Crops (Arundo, Switch- grass, Miscanthus Fiber Sorghum); Ag Residues (Rye Straw)	Active Development (Start-up planned 2015)	Proprietary pre-treatment (PROESA TM) + Viscosity reduction + enzymatic hydrolysis + Fermentation (C5 and C6) www.chemtex.it
Cobalt Technologies	Mountain View, CA	Commercial (Biochemical)	Biobutanol	n.a	Bagasse and waste wood	Announced to build a commercial plant in Brazil 2015 for sugarcane bagasse to biobutanol.	Proprietary dilute acid hydrolysis pre-treatment and enzymatic hydrol- ysis process http://www.cobalttech.com/
Codexis, Inc.	Redwood City, CA	Biochemical	CodeXyme TM cellu- lase enzymes	n.a	n.a	n,a	Cellulase enzyme developing company http://www.codexis.com/

Ammonium hydroxide based pre- treatment, enzymatic hydrolysis process (Genencor enzymes) and Zymomonas fermentation http://www2.dupont.com/BioFuel/ en_US/index.html	The project would combine Beta's PROESA pre-treatment technology and Gevo's proprietary fermentation process for biobutanol production.	Gas fermentation, acquisition of the former Range Fuels biorefinery on January 3, 2012 http://www.lanzatech.com/	Single-step fermentation, proprietary biocatalyst http://www.ls9.com/	Proprietary consolidated bioprocessing (CBP) technology http://www.mascoma.com/	Proprietary, leading EDGETM (Efficiency Directed Genome Engineering) technology platform enables rapid, rational, and robust optimization of microbes and bioprocesses to efficiently produce fatty acids and manufacture bioproducts, OPXBIO is working with The Dow Chemical Company to bring BioAcrylic into the market. http://www.opxbio.com/	
Ammonium hydroxide bas treatment, enzymatic hyd process (Genencor enzym Zymomonas fermentation http://www2.dupont.com/en_US/index.html	The project wou PROESA pre-tre ogy and Gevo's mentation proce production.	Gas fermentation former Range Full January 3, 2012 http://www.lanza	Single-step ferments biocatalyst http://www.ls9.com/	Proprietary consolidating (CBP) technology http://www.mascoma	Proprietary, leading EDGE (Efficiency Directed Genon Engineering) technology penables rapid, rational, and optimization of microbes a bioprocesses to efficiently fatty acids and manufactur bioproducts. OPXBIO is working with The Dow Chemical Company to BioAcrylic into the market.	
Commercial operation by Mid-2014	Commercial production in the first half of 2012	commercial operation in 2013	Announced the successful start-up of Florida demonstration Facility on Sept. 10, 2012	Commercial operation in 2015	Successfully demonstrated its fermentation process for BioAcrylic at the 3,000-liter scale at the Michigan Biotechnology Institute (MBI) in Lansing, Mich. in Oct 2012.	
Agricultural biomass e.g. corn stover, switchgrass	Multiple feedstocks	Forest Residue	Sweet sorghum syrup, Biomass hydrolysate	Wood pulp and chips	Sugars	
• 113.6 ML/y (30 MGPY) commercial	 Bioethanol 83.28 ML/y (22 MGPY) Isobutanol 68.14 ML/y (18 MGPY) 	• 15.14 ML/y (4 MGPY)	• 37.85 ML/y (10 MGPY)	 Pilot 0.757 ML/y (0.2MGPY) Commercial 75.71 ML/y (20 MGPY) 	n.a	
Bioethanol	Isobutanol	Bioethanol Biochemicals	Fatty alcohols	Bioethanol	Bio-based chemicals and fuels e.g. diesel Electrofuel, BioAcrylic	
Demo & commercial (Biochemical)	Demo (Biochemical)	Demo (Hybrid)	Demo (Biochemical)	Pilot/Demo (Biochemical)	(Biochemical)	
Vonore, TN (Demo) Nevada, IA (commercial)	St. Joseph, MO (Demo) Luverne, MN (Commercial)	Soperton, GA	Okeechobee, FL	Rome, NY (pilot/demo) Kinross, MI (commercial)	Boulder, CO	
DuPont Biofuels Solution	Gevo	LanzaTech	FS9	Mascoma	OPX Biotechnologies, Inc.	

	Short Notes on Process and Additional Information - Other remarks (web site)	or Acid Hydrolysis/CASE TM process, aims concentrated hydrochloric acid hydrolysis followed by separation of and purification of sugars. 000 http://www.virdia.com/sing		inta- Proprietary three-step process syn- ouse gas fermentation ated http://www.coskata.com/ ,000	I Patented bacteria for syngas in fermentation http://www.ineos.com/ bilot ition	pper- Biomass to Alcohol followed by cat- alytic upgradation to green gasoline/ jet fuel/diesel, Partnership with LanzaTech for the fermentation phase www.swedishbiofuels.se	pper- Proprietary process, acetic acid via agin- fermentation then converted to ethyl acetate followed by hydrogenation to ethanol.
	Status	By late 2014 or early 2015, it aims to build commercial plant of capacity 500,000 tons (1 B lb) biomass processing per year.		Syngas fermentation at Lighthouse has accumulated more than 15,000 operating hours.	i. Commercial plant starting in 2013. ii. Integrated pilot plant in operation since 2003.	Commercial operation from 2014	Commercial operation in the beginning of 2015
	Feedstock	Woody Biomass	emical)	Mixed feedstock, wood biomass, and municipal solid waste	i. Vegetative, yard and citrus waste ii. micxed lignocel- lulosic biomass	Green biofuels from biomass, including grain crops, agricultural waste, wood and forestry waste	Poplar trees, Wheat straw
	Installed Capacity	n.a	Hybrid (Thermochemical & Biochemical)	n.a	i. Commercial 30.8 ML/y, (8 MGPY) bioethanol and 6 MWe Power ii. 1.5 t/d biomass processing	20,000 Mt/y of biomass at commercial facility	Demo 0.25 MGPY Commercial 25+ MGPY
	Product(s)	Cellulosic Sugar, Lignin	Hybri	Bioethanol	Bioethanol Renewable power	Renewable diesel,	Bioethanol, Biochemicals
	Type (Technology)	Pilot/Demo (Biochemical)		Semi-commercial facility (Hybrid: Thermo- bio-chemical)	Pilot & commercial (Hybrid: Thermobio-chemical)	Demo (Hybrid:Thermo- Bio-chemical)	Demo (Hybrid: Thermo- bio-chemical)
inued)	US Site	Danville, VA		Madison, PA Warrenville, IL	i. Vero Beach, FL (Commercial) ii. Fayetteville AK (Pilot)	USA	Boardman, OR
Table 1. (Continued)	Company Proj/Acron.	Virdia (formerly HCL CleanTech)		Coskata	INEOS Bio	Swedish Biofuels, AB	ZeaChem

Table 2. Biofuels	s commerciali	Table 2. Biofuels commercialization activities in the EU.	in the EU.				
	EU Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
				Thermochemical	sal		
BFT Bionic Fuel Technologies <i>Bionic</i>	EU - Aarhus (DK)	Demo (Thermochemical- microwave)	Diesel hydrocarbons	• 25 kg/h	50 kg/h ligno- cellulosic, straw pellets	Interrupted	Started up in 2008 Catalytic (zeolite) low temperature de-polymerization of hydrocarbon through microwave technology http://www.bionic-world.net
	EU - Skärblacka (SE)	Demo (Thermochemical)	Pyrolysis Oil	• 160,000 t/year of pyrolysis oil	720 dry ton/day of lignocellu- losic biomass		biomass pre-treatment (both before and after drying), biomass drying, flash pyrolysis process including condenser, and storage of pyrolysis oil 31.4 M€ funding from NER 300
BioMCN, Siemens, Linde, VS Hanab Woodspirit (NER300)	EU - Oosterholm, Farmsum (NL)	Commercial (Thermochemical)	Biomethanol	• 516 MI/y Biomethanol (413,000 t/y)	1.5 Mt/y of imported wood chips	Planned	Thermochemical torrefaction + entrained flow gasification to biomethanol; 199 M€ funding from NER 300 http://www.biomcn.eu
	EU - Hengelo (NL)	Demo (Thermochemical)	Electricity Process Steam Fuel oil Organic acids	25 MWth polygeneration unit3.2 t/h oil6 MW steam800 kWe power	Woody biomass (5 t/h - 43,000 t/y)	Expected to start begin-ning 2013	Flash pyrolysis (rotating cone technology) + oil stabilization and acetic acid recovery www.btg-btl.com; www.empyroproject.eu www.biocoup.com; www.btgworld.com
	EU - Piteå (SE)	Demo (Thermochemical)	DME	• 4 t/d DME	Black liquor	Operational since 2010	BL gasification + gas conditioning + biomethanol synthesis + DME synthesis and purification. Test fleet (10 trucks) achieved 750,000 km (October 2012) Another project Currently waiting for new national regulation on biofuels could be located at Domsjö and Vallvik mills: ~200 MWt / Methanol and DME (On hold) http://chemrec.se/
	EU - Freiberg (DE)	Demo (Thermochemical)	FT-fuels (BtL Diesel- SunDiesel [®] , Naphta)	• 13,500 t/y (18 Ml/y, 4.76 MGPY)	Lignocellulosic biomass, dry wood chips (recycled wood and residual forestry wood)	Project interrupted	Three stage gasification (low temperature gasification + high temperature gasification + endothermic entrained bed gasification) + dust removal + gas shift reactor + scrubber + FT reactor + upgrading. IT used SMDS (Shell Middle Distillate Synthesis) technology On 9 February 2012 Choren's biomass gasification technology was sold to Linde Engineering Dresden, who will further develop the Choren Carbo-V® technology used to produce syngas. (www.biofuelstp.eu/btl.html) www.choren.com

Table 2. (Continued)	(pen						
Company <i>Proj.Acron.</i>	EU Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
EON Bio2G	EU - Rya Harbour (SE)	Demo (Thermochemical)	Syngas Power Heat	• 200 MW, ~21 000 Nm³/h biogas, 62-63% SNG efficiency • 10 MW power • 50 MW Heat	325 MWth lignocelllosic biomass	Construction planned to start in 2013. Expected start-up end 2015	Total Efficiency 70-80% http://www.eon.se/om-eon/Om-energi/Energikallor/ Energigas/Biogasfornybar-energi/Bio2G/
GOTEBORG Energy AB GoBiGas	EU - Rya Harbour (SE)	Demo (Thermochemical)	Syngas Thermal power to DH	• 24.5 MWth producer gas> 20 MWth SNG • 2.5 MWth thermal power gasification (to DH) + 1.3 MWth thermal power SNG	32 MWth of forest residues, wood pellets, branches, tree tops	Under construction, start-up 2013	Demo Start-up planned by 2013 Indirect gasification (Repotec/Metso Power) + fixed bed methanation (Haldor Topsoe); Excess heat to District Heating
GoBiGas2 (NER300)	EU - Rya Harbour (SE)	Commercial (Thermochemical)	Commercial SNG Thermal power to DH	• 800 GWh/y SNG	500,000 t/y wet lignocellulosic biomass	Completion of the initial BoBiGas project. Planned by 2015	High quality synthetic natural gas (SNG) by indirect gasification at atmospheric pressure (FICFB, Repotec/Metso Power), gas cleaning, methane production (via nickel catalyst), pressurization and injecting the product into the regional gas network 100 MW installed capacity 58.8 M€ funding from NER 300 www.gobigas.se www.coptec.at/index.php/97.html
KIT Karlsruhe Institute of Technology BIOLIQ	EU - Karlsruhe (DE)	Pilot (Thermochemical)	Pyrolysis oil (bioliq- Syncrude®) Syngas DME Gasoline (MTG process)	 1,000 kg biosyn-crude (5 MWth) 700 Nm3/h gas purification 50 kg/h DME 30 kg/h Gasoline 	500 kg/h bio- mass (2 MWth)	Under	Planned by 2013 5 stage plant MTG: fast pyrolysis + entrained flow gasification + gas purification + DME synthesis + gasoline synthesis www.bioliq.de
Metso /Fortum/UPM	EU – Joensuu (Fl)	Demo (Thermochemical)	Pyrolysis oil	• 50 000 t/y	Forest residues	Construction started, start-up planned for Q4 2013	The solution has been under development by Metso Power, in partnership with Fortum, UPM and VTT, since 2007
Metso /VTT	EU – Tampere (FI)	(Thermochemical)	Pyrolysis oil	• 70 m³ produced by May 2010	Forest residues	Operational since 2009	Synthetic fuel via gasification + fermentation (gasification, fermentation, and purification) www.metso.com; www.vtt.fi; www.upm.com

Neste - StoraEnso	EU - Varkaus (FI)	Pilot (Thermochemical)	Synthetic diesel over direct biomass gasification	• n.a.	Forest residues	Started up in 2010	Abandoned in 2012 Biomass drying + gasification + gas cleaning and testing of FT catalysts. Aimed at develop technologies and engineering solutions for a commercial-scale plant.; 12 MW gasifier included in the project http://www.nesteoil.com/
TUW	EU - Guessing (A)	Pilot (Thermochemical)	FT-liquids	0.2 t/y FT-liquids	7 Nm³/h syngas from lignocellu- losic biomass	Operational since 2005	RME scrubbing + compression + cleaning (fixed bed reactors for chlorine and organic sulfur removal; as an alternative, an activated charcoal filter is used) + slurry reactor (at 25 bar) Partner: REPOTEC www.ficfb.at
ThyssenKrupp- Uhde BioTFuel	EU - (FR)	Commercial (Thermochemical)	FT products from mix of biomass and fossil fuels	Biodiesel, biokerosene	Mix of fossil and biomass fuel, including torre- fied biomass	Commercial plant in 2017	Commercial 12 MW thermal PRENFLO-PDQ pressurized gasifier (1200-1600 °C, 30-40 bar, 3-5 s resident time) 113 Mio € incl. total subsidies of 33 Mio € from French Public Funds
Värmlandsme tanol	EU -Hagfors (SE)	Pilot (Thermochemical)	Pilot Biomethanol District heating	Pilot • 300 t/day BioMeOH • 15 MW DH	Pilot ~25 t/h of domestic forest residue	Pilot 2014	111 MWth HTW pressurized fluidized bed gasifier (800-1000°C, 10-30 bar, biomass size < 4 mmm) http://www.thyssenkrupp-uhde.de
ThyssenKrupp- Uhde BioTFuel	EU - (FR)	Commercial (Thermochemical)	FT products from mix of biomass and fossil fuels	Biodiesel, biokerosene	Mix of fossil and biomass fuel, including torre- fied biomass	Commercial plant in 2017	Commercial 12 MW thermal PRENFLO-PDQ pressurized gasifier (1200-1600 °C, 30-40 bar, 3-5 s resident time) 113 Mio € incl. total subsidies of 33 Mio € from French Public Funds
Värmlandsme tanol	EU -Hagfors (SE)	Pilot (Thermochemical)	Pilot Biomethanol District heating	Pilot • 300 t/day BioMeOH • 15 MW DH Biochemical	Pilot ~25 t/h of domestic forest residue	Pilot 2014	111 MWth HTW pressurized fluidized bed gasifier (800-1000°C, 10-30 bar, biomass size < 4 mmm) http://www.thyssenkrupp-uhde.de
Abengoa	EU - Babilafuente (ES)	Demo (Biochemical)	Bioethanol Power	• 5 MI/y EtOH (1.32 MGPY)	35,000 t/y cereal straw (barley, wheat)	In operation since 2009	EH (Glucose), steam explosion - Over 6,000 h operation http://www.abengoa.com
BIOAGRA CEG Plant Coswinowice (NER300)	EU - Coswinowice (PL)	Commercial (Biochemical)	Bioethanol Lignin Biogas	O MIl/year EtOH To,000 t dry lignin (moisture content 50-60%) biogas (22.3 MNm³ biogas, 75% methane)	~250000 t/year of wheat straw (75%) and corn stover (25%)	Planned	BIOAGRA is owned by 49% of the polish Company BIOAGRA Bioagra produces 140,000 cubic meters of ethanol and 100,000 tons of DDGS (animal feed) annually from grain as the raw material. 30.9 M€ funding from NER 300 http://www.bioagra.pl/index.php?Lng=eng http://www.sekab.com/about-us/facilities/bioagra

Table 2. (Continued)	(panu						
Company Proj. Acron.	EU Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
BIOGASOL Maxifuels	EU - Techn.Un. Denmark DTU (DK)	Pilot (Biochemical)	Bioethanol Hydrogen, Methane Lignin rich stream	60 kg/h pre-treatment 20 kg/h hydrolysis and fermentation	30 kg/h Various	Completed	Proof of concept (Carbofrac TM) in operation August 2006 - August 2008 C5 and C6 fermentation (Pentoferm TM) Wet oxidation: 180 °C-20 bar, addition of O2 and water EtOH effluent converted to biogas, detoxification of process water 30 kg/h pre-treatment (pre-treated biomass ~30 % DM) www.biogasol.com
BlOGASOL Bombiofuel1	EU - Ballerup (DK)	Pilot (Biochemical)	Bioethanol Hydrogen, Methane Lignin rich stream	• 50 kg/h pre-treatment • 250 I C5 fermenta- tion + 2500 I C5 fermentor	500 kg/h Various	Completed	Achieved sustained productivities of >1 g/l/h. Achieved 1 g/l/h C5 EtOH in 2.5 $\rm m^3$ reactor, high yields >0.42 g EtOH / g sugar and >80% conversion rates (280-350 l/t dry biomass). Low toxicity at ~500kg/h. More than 10 feedstock's tested
Bornbiofuel2	EU - Lervangen, Taastrup (DK)	Demo (Biochemical)	Bioethanol Hydrogen, Biogas (CH4) Lignin rich stream	• 5 MI/y EtOH • 4 t/h pre-treatment	2.5 t/h Grasses, garden waste, straw	Ongoing	Initially planned by end 2011. Rescheduled 2012-2014. www.biogasol.com
BORREGAARD BALI	EU - Sarpsborg (NO)	Pilot (Biochemical)	Fermentation to Bioethanol (C6) Chemicals, Yeasts (C5) Performance Chemicals from (water soluble) Iignin	Sugars, Ethanol, Chemicals	Multi-feedstock - Lignocellulosic biomass (~2 t/d, 30-100 kg/h)	Started-up 2012	BALI TM neutral or acid process Lignin processing + continuous polysaccharide hydrolysis (high solid loading) + fermentation Sulfonated lignin (lignosulfonate) www.borregaard.com
Chempolis	EU - Oulu (FI)	Demo (Biochemical)	Bioethanol Pulp Biochemical as by products	• 5,000 t/y Biothanol	25,000 t/y non- wood lignocel- lulosic biomass	Operational	Lignocell. Bioethanol and biochemical: formicobio TM process Pulp (fibers) for paper: formicofib TM process www.chempolis.com
CHEMTEX/ M&G/Beta	EU - Rivalta (IT)	Pilot (Biochemical)	Bioethanol	• 250 kg/d Biothanol • Pre-treated biomass	1 t/d of straw, Arundo Donax, other lignocellulosic biomass	Operational since 2009	Proprietary pre-treatment (PROESA TM) + Viscosity reduction + EH + Fermentation (C5 and C6) A large number of different feedstock's tested
FP7-Biolyfe (NER300 - BEST)	EU - Crescentino (IT)	Demo (Biochemical)	Bioethanol Power	• 40,000 t/y Biothanol • 13 MWe	180,000 dry t/y of straw, Arundo Donax, other lignocellulosic biomass	Under commissioning, start up beginning 2013	Proprietary pre-treatment (PROESA TM) + Viscosity reduction + EH + Fermentation (C5 and C6) Also selected by the NER300 first round, with a support of 28,4 M£

<i>FP7-</i> CОМЕТНА	EU - to be defined (IT)	Commercial (Biochemical)	Bioethanol Power	• 80,000 t/y Biothanol	360,000 dry t/y of straw, Arundo Donax, other lignocellulosic biomass	Construction planned 2015-2016	PROESA TM Technology is licensed by Beta Renewables www.betarenewables.com; www.chemtex.it
CLARIANT (Süd-Chemie) Sunliquid®	EU – Munich (DE)	Pilot (Biochemical)	Bioethanol Lignin	• 1 t/y EtOH	4,5 t/y wheat straw or other agricultural residues	Inaugurated February 2009	Biomass pre-treatment + hydrolysis and fermentation, with integrated enzyme production www.clariant.com
CLARIANT for- merly Süd-Chemie Sunliquid [®]	EU - Straubing (DE)	Demo (Biochemical)	Bioethanol Lignin (used for energy generation) Biogas Fertilizers	• 1,000 t/y EtOH	4,500 t/y wheat straw or other agricultural residues, energy crops	Inaugurated July 2012	EH (integrated enzyme production); Feedstock & process specific enzymes; Simultaneous C5-C6 fermentation Energy saving adsorption-based separation technology process yield of 20 - 25% (theoretic EtOH-yield of 27% for wheat straw) www.clariant.com
IMECAL	EU - L'Alcudia, Valencia (ES)	Pilot (Biochemical)	Bioethanol	• 4 MI/y EtOH (1.06 MGPY) (11,200 I/d EtOH)	70 t _{MSW} /d (organic fraction)	Operational	160 l _{ErOH} /t feedstock (aiming at 220 l _{ErOH} /t) Pre-treatment: physical (elimination of plastics, metal and glass; trituration) + acid hydrolysis EH, SSF 8 www.imecal.com
INBICON - DONG Energy	EU - Fredericia (DK)	Pilot (Biochemical)	Bioethanol C5 molasses Lignin rich stream	• n.a.	Straw and ligno- cellulosic bio- mass (0.1 t/h)	Operational since 2003	Hydrothermal pre-treatment + EH + fermentation http://www.inbicon.com
INBICON - DONG Energy Kacelle	EU - Kalundborg (DK)	Demo (Biochemical)	Bioethanol C5 molasses Lignin rich stream	 5.400 MI/y (1.43 MGPY, 4,300 t/y) Lignocell EtOH 11,250 t/y molasses (70% DM) 	30,000 t/y wheat straw	Operational since 2009	Yield of ethanol > 180 I EtOH/ton straw (86% DM) High dry matter in pre-treatment (35%) and hydrolysis (25% WIS) (same low enzyme dosage as in pilot scale used) http://www.inbicon.com
PROCETOL 2G Futurol	EU - Pomacle (FR)	Pilot (Biochemical)	Bioethanol	• 180,000 l/y (47500 GPY, ~500 l/d)	Lignocellulosic, various	Inaugurated October 2011	EH + fermentation Scale up expected by 2015 (prototype 3,500,000 I/y) and by 2016 (industrial 180,000 I/y) www.projet-futurol.com
SCHWEIGHOFER FIBER Gmbh	EU - Hallein (A)	Demo (Biochemical)	Bioethanol	• 12,000 t/y	500,000 t/y sulfite spent liquor from pulp mill digester (33% dry content)	Plant postponed	Ethanol concentration after fermentation of sugar- containing liquor: 2% www.schweighofer-fiber.at

Table 2. (Continued)	tinued)						
Company <i>Proj.Acron.</i>	EU Site	Type (Technology)	Product(s)	Installed Capacity	Feedstock	Status	Short Notes on Process and Additional Information - Other remarks (web site)
0 Z F	EU - Zeis (NL)	Pilot (Biochemical)	Steam pre- treated biomass	• 50 kg/h pre-treated biomass	13 kg/h whet straw, corn stover, bagasse, wood chips, other lignocellulosic biomass	Operational since 2002	Superheated steam exchange heat with biomass by convection rather than condensation as in steambased pre-treatment systems. Very high initial dry matter content: 20-45% and higher (thus, lower energy and less acid catalyst demand). Good process control as fast increase/decrease of T is possible; Fermentation of samples at 38% DM successfully carried out
UPM FiberEtOH	EU – N/A	Demo (Biochemical)	Bioethanol Biogas green electricity Sludge as fuel	• 15 MI/y EtOH (3.96 MGPY) • Biogas green electricity 60 GWh/a • Sludge for fuel 100 000 t /a	170 000 t SRF/a	Decision	Commercial & Industrial waste pulping and pulp preparation for ethanol production Fiber hydrolysis and fermentation to produce ethanol (yield 200 liters/dry tons of fiber); Biogas production from distillation stillage Sludge drying after biogas production to prepare solid biofuel for CHP www.upm.com
VERBIO (NER300)	EU - Schwedt (DE)	Demo (Biochemical)	Biogas- Biomethane	• 25.6 Mm3(s)/y, containing 12.8 Mm3(s)/y biomethane	7,000 t/y straw	Planned	Main process phases: raw material handling, biomass pre-treatment of biomass by steam and enzyme successively, production of biogas by anaerobic fermentation, and biogas post-treatment and upgrading to biomethane and grid injection. 22.3 ME funding from NER 300 http://weyland.no
WEYLAND	EU - Blomsterdalen (NO)	Pilot (Biochemical)	Bioethanol, lignin, sugars	• 158 kg/y	75 kg/h of ligno- cellulosics; vari- ous feedstocks, mainly spruce & pine	In operation since 2010	Process based on concentrated acid hydrolysis of lignocellulosic biomass. Pre-treatment based on how water and < a bar steam. Fermentable sugars achieved in less than 5 hours with low level of inhibitors.

Legend: **BL**: Black Liquor; **CHP**: Combined Heat and Power (cogeneration); **CTO**: Crude Tall Oil; **DH**: District Heating; **DM**: dry matter; **DME**: DiMethylEther; **EtOH**:Ethanol; **FT**: Fischer-Tropsch; **HC**: Hydrocarbons; **MeOH**: Methanol; **MSW**: Municipal Solid Waste; **MTG**: Methanol To Gasoline; **NER300**: EC funding programme (decision on first list of project taken on 18 Dec.2012); **SSF**: Simultaneous Saccharification and Fermentation; **RME**: RapeMEthylEsther; **SSCF**: Simultaneous Saccharification and Co-Fermentation; **SNG**: Synthetic Natural Gas; **t**: dry tons; **T**: temperature; n.a.: not applicable.

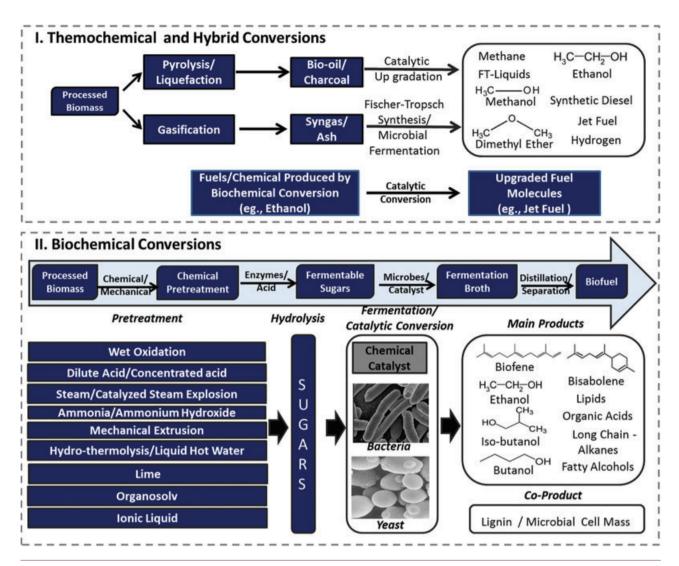


Figure 1. Different biomass conversion routes used in the industry. Here, I, Thermochemical and Hybrid Conversion; II, Biochemical and Hybrid Conversion and III, Hybrid conversion are given.

industrial projects have adopted biochemical conversion methods. The biochemical route is followed mainly for the production of bioethanol using pre-treatment of biomass followed by fermentation. Some of the projects are also pursuing other advanced biofuels such as long chain liquid hydrocarbons (Amyris) and biobutanol (Butamax, Cobalt, and Gevo) using their innovative and proprietary technologies.

Intermediate to the research and industrial initiatives, Michigan Biotechnology Institute (MBI), which is a part of Michigan State University (MSU), is working toward scaling up and commercializing ammonia fiber expansion (AFEX^{TM*}) pre-treatment through a US\$4.3 million grant from the DOE. A one ton-per-day pilot AFEX reactor is

currently being installed. In 2013 another US\$2.5 million DOE grant was awarded to Novozymes and MBI in partnership, to examine the use of AFEX-pre-treated biomass as a feedstock for enzyme production.

Thermochemical routes include pyrolysis, liquefaction, and gasification, and are used to produce long chain liquid hydrocarbons (Fig. 1). Hybrid routes (i.e. combined thermochemical and biochemical) are used for producing both bioethanol and long chain liquid hydrocarbons. As shown in Table 1, the thermochemical platform has been adopted by 14 industries, 5 of which are pursuing hybrid routes. Swedish Biofuels' approach is interesting in that it first produces bioethanol via the conventional biochemical route and then catalytically upgrades it to 'drop-in' biofuels. Similarly, Zeachem's approach is to produce lactic acid though fermentation and subsequently upgrade it to

^{*}AFEXTM is a registered trademark of MBI International, Lansing, MI.

bioethanol via hydrogenation. Coskata, Ineos Bio, and Lanza Tech's process strategies depend on syngas (CO + $\rm H_2$) fermentation to bioethanol using their proprietary micro-organisms. The projects reported in Table 1 are not exhaustive and include only those industries whose project details are publicly available. There are several other US projects that are developing some innovative technologies to produce advanced biofuels but are maintaining a very low profile or operating in stealth mode because of their business strategy.

In addition to the single company commercial ventures listed above, technology evaluations are often done through industrial partnerships. A number of partnerships currently exist between Beta/Chemtex/M&G and Genomatica (renewable chemicals, as bio-butadiene BD and bio-butanediol BDO), Gevo (integrated process for bio-isobutanol production), Amyris (renewable fuels and chemicals, as bio-farnasene/farnasano) and Codexis (second-generation detergents from cellulosic biomass), in which the pre-treatment process is combined with various technologies and know-how provided by the partners.

EU projects

With regard to EU initiatives in the field of lignocellulosic biofuels, out of the 40 EU projects reported in Table 2, 17 are based on the thermochemical process, 22 on the biochemical process, and 1 is based on a chemical approach (we identified a total of 5 projects for the chemical route, but only one from a lignocellulosic feedstock). This includes the new projects, either thermochemical or biochemical, recently selected for support by the EC through the NER300 program, 5 of which were for lignocellulosic liquid fuels, and the remaining on lignocellulose-derived biomethane/syngas or intermediate energy liquid carrier (pyrolysis oil, so far targeting district heating). No project was identified in EU as hybrid process technology.

In the field of biochemical conversion, several plants with the capacity to generate thousands or tens of thousands of tons of product per year exist or are under development in the EU. One of the very first EU industrial demonstration initiatives (by Sekab) has been interrupted, but several other processes have been successfully developed into demonstration scale plants. Among these, the largest industrial scale-up efforts are being carried out by Abengoa, Biogasol, Borregaard, Chempolis, Chemtex/M&G (licensed by Beta Renewables), Clariant, Dong Inbicon, Clariant, IMECAL, Inbicon/Dong, Schweighofer Fiber, and UPM.

The situation for thermochemical technologies appears to be slightly different. The largest EU projects aimed

at Fischer-Tropsch (FT) products from lignocellulosic biomass (such as Choren or Neste StoraEnso) have been abandoned or interrupted for various reasons. Today the most relevant initiative is one by Metso/Fortum, a demo project which mainly aims at producing energy rather than a second-generation transport fuel from lignocellulosic biomass. However, the number of initiatives in the thermochemical area focused on generation of transportation fuels could significantly expand if the BTG/Empyro, UPM/Stracel/Btl, VAPO/Ajos-Forest Btl, Billerud/Pyrogrot, CEG plant Coswinowice/Bioagra, BioMCN/Woodspirit, Goteborg AB/Gobigas2, Chemrec and KIT Bioliq projects move toward demonstration-scale. The recent NER300 decision allocated ~€457 million to liquid biofuels produced by the thermochemical route and ~€59 million to the biochemical route, corresponding to only three projects: two using hydrolysis and fermentation and one using anaerobic digestion. This is expected to give a considerable jumpstart to thermochemical pathway technologies. Other than FT-liquids (especially diesel), DME is a major product addressed through the thermochemical pathway. Conversion of biomass to other energy sources such as gasoline (MTG), hydrogen, and natural gas are also under investigation. Synthetic natural gas is another area of fast growth and innovation in the EU and was developed as a method for upgrading CO₂ and H₂ to synthetic CH₄ using energy from fluctuating sources (photovoltaic PW, wind). Goteborg AB GoBiGas project is one example of a demo SNG project of a relatively large size.

Several of the EU-based conversion processes are also going to be implemented in the US or outside the EU, either as first installments or as replications or extensions of an EU demo unit. This is the case of Abengoa, M&G/Chemtex, Swedish Biofuels, and British Airways/Solena. This confirms that industrial development of second-generation biofuels in a given region can have wide-ranging global impacts.

A total of 31 and 35 biofuels projects using lignocellulosic biomass as a feedstock are listed in Table 1 (US) and Table 2 (EU), respectively. It appears that the biochemical conversion platform dominates (18 projects) the commercialization activities in the US and the majority (10 projects) of these projects are aimed toward commercial production of bioethanol by the year 2015. There are seven ongoing projects in the US that are mainly focused on producing liquid hydrocarbon fuels. It is interesting to note that four US projects have adopted a hybrid route whereas there are no active projects in the EU that use this pathway to produce biofuels from lignocellulosic biomass.

The EU projects are almost equally distributed between thermochemical (17 projects) and biochemical

(18 projects) conversion platforms. This shows that the biochemical pathway and bioethanol production may be the preferred route in the US, but EU commercialization activities do not show an obvious preference.

Lignocellulosic feedstock for the biorefinery

Available biomass in the US

North America is comprised of 23 countries with roughly 16.5% of the global land area. The USA is one of the biggest

countries in North America with an area of 3.79 million square miles. (9.83 million km²), or nearly 2263 million acres of which the composition is 33% forest land, 26% pasture grassland, 20% crop land, 8% parks and recreation area used by public, and 13% urban areas, swamp and desert. Of the total available land, nearly 60% of the land has the potential to grow different biomass depending on the soil conditions. Both the DOE and the US Department of Agriculture (USDA) are developing and funding biomass-to-energy programs. By doing this, it is widely believed that the twenty-first century will see several biorefineries that produce a variety of fuels and chemicals

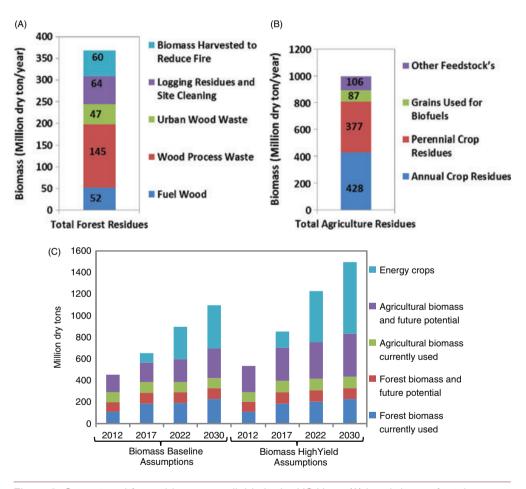


Figure 2. Current and future biomass available in the US Here, (A) breakdown of total available forest residue by 2030 based on 2005 study;²¹ (B) breakdown of total available Agricultural residue by 2030;²¹ and (C) summary of current use and future total potential biomass based on baseline assumptions and high yield assumptions based on 2011 study.²² There are subtle differences in the assumptions between the 2005 *Billion Ton Study* and 2011 *Son of Billion Ton Study*. The 2011 study did include county-level analysis with aggregation to state, regional, and national levels that include 2009 USDA agricultural projections and 2007 forestry RPA/TPO 2012–2030 timeline. Biomass annual projections are based on a continuation of baseline trends (USDA projections) and changes in crop productivity, tillage, and land use.

using biomass from agricultural and forest residues. Development of clean, reliable, and affordable energy technologies will strengthen the nation's energy security (less dependence on foreign oil), have positive environmental benefits (reduced GHGs) and strengthen the economy (by generating jobs in the rural sector).^{5,20}

The Energy Independence and Security Act (EISA) of 2007 set up a mandatory Renewable Fuels Standard (RFS) to achieve 36 billion gallons per year (BGY) of biofuels by 2022. Only 15 billion gallons can come from corn ethanol and the remaining 21 billion gallons of advanced biofuels should come from non-corn starch based feed stocks (e.g. sugars or cellulose). To meet the targets set by the mandate, not only do sufficient production facilities need to be constructed, but also sufficient quantities of biomass need to be generated and available. The DOE Office of the Biomass Program and Oak Ridge National Laboratory attempted to answer the question of how much biomass was available and where was it located with a report in 2005, 21 often called the Billion Ton Study, and later with an update report in 2011.²² These reports estimated that there is ~1.3 billion tons of biomass/year available in US alone by 2030 based on reasonable assumptions. Of this, 368 million dry tons will come from forest resources

including: (i) fuel wood harvested from forest (52 million), (ii) wood process mill residues and pulp and paper mill waste (145 million), (iii) urban wood waste from construction and demolition debris (47 million), (iv) residues from logging and site cleaning operations (64 million), and (v) biomass that could be harvested to reduce fire (60 million) (Fig. 2(a)). The remaining 998 million tons will come from agricultural resources that include: (i) annual group residues (428 million), (ii) perennial crops (377 million), (iii) grains used for biofuels (87 million), and (iv) animal manure, process residues and other feedstock's (106 million) (Fig. 2(b)). In order to estimate the amount of biomass that will be available in 2030, we need to consider two different assumptions: (i) with moderate crop yields and (ii) with high crop yields (Fig. 3(c)). In both assumptions, energy crops that are currently being developed by several biotech companies in the US (Ceres, Thousand Oaks, CA; Mendel, Hayward, CA; Monsanto, St Louis, MO) will play an important role in meeting the projected estimates. Energy crops will be made available only if the state or federal government give incentives to farmers to grow them or the companies have a buy back guarantee contract with the farmers or group of farmers (co-op). The biomass residues coming from the agriculture sector are

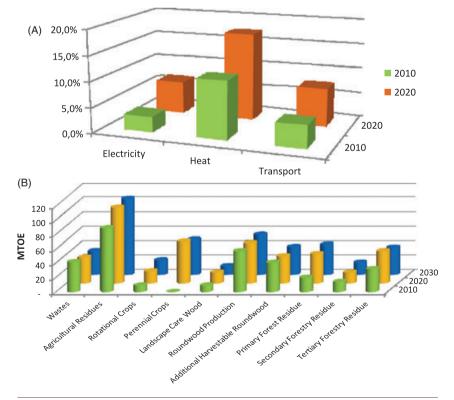


Figure 3. (A) EU27: Share of biomass in total final energy consumption and (B) Current and 2020–2030 potential for reference scenario.²⁴

about three-quarters of the total available resources in the US. These have high potential for improvement by using advanced farm management technologies, using superior plant breeds, and by adopting best agricultural practices (growing cover crops, crop rotation, growing perennial crops on marginal land, etc). Removal of agricultural residues from the field could vary depending on the soil condition, as the removal rate must maintain soil quality. Agricultural residue availability has been calculated based on five different scenarios, each with a different assumption (low/high crop yield and with/without land use change). These scenarios include: (i) currently available from agricultural lands, (ii) under moderate crop yield increase without land use change, (iii) under high crop

yield increase without land-use change; (iv) under moderate crop yield increase with land-use change, and (v) under high crop yield increases with land-use change (Table 3). Dedicated energy crops (switchgrass, Miscanthus, energy cane, forage sorghum, *Erianthus*, Napier grass, etc.,) will contribute significantly to satisfy the growing demand of agricultural residues. Many companies are taking a leading role in establishing businesses in these sectors.

Biomass available in Europe

Based on Fig. 3(a), from the 27 EU member states National Renewable Energy Action Plans (NREAPs), biomass is expected to play a major role in achieving EU targets on renewable energies. It has been projected that 12% of total

Sorghum 0.0 2.8 4.0 1.3 4.0 5.0 6.8 9.7 6.8 9.7 12.4 11.4 12.9 11.4 12.9 Barley 0.7 0.0 4.7 2.8 4.7 3.1 5.0 7.2 5.0 7.2 7.7 8.3 9.6 8.3 9. Oats 0.1 0.7 1.2 0.7 1.2 1.3 1.8 2.5 1.8 2.5 3.2 3.0 3.3 3.0 3. Wheat (winter) 8.8 27.4 44.9 27.4 40.9 24.0 46.0 66.6 46.0 60.6 60.1 76.7 88.8 76.7 80. Wheat (winter) 2.2 7.4 10.9 8.0 15.7 22.7 15.7 20.3 20.1 26.2 30.3 26.2 27. Soybean 0.0 0.0 0.0 12.7 47.9 46.3 76.8 104.5 102.4 123.7	Table 3. E	Breakd	own of	agricu	ultural	residu	e avail	ability	in the	US bas	sed on	five di	fferent	scena	arios. ²²	
Corn 74.8 169.7 256.1 169.7 256.1 90.0 187.9 281.8 187.9 281.8 225.0 313.1 375.7 313.1 375. Sorghum 0.0 2.8 4.0 1.3 4.0 5.0 6.8 9.7 6.8 9.7 12.4 11.4 12.9 11.4 12.2 Barley 0.7 0.0 4.7 2.8 4.7 3.1 5.0 7.2 5.0 7.2 7.7 8.3 9.6 8.3 9.0 Oats 0.1 0.7 1.2 0.7 1.2 1.3 1.8 2.5 1.8 2.5 3.2 3.0 3.3 3.0 3.3 Wheat (winter) 8.8 27.4 44.9 27.4 40.9 24.0 46.0 66.6 46.0 60.6 60.1 76.7 88.8 76.7 80. Wheat (winter) 2.2 7.4 10.9 8.0 15.7 22.7 15.7		Biom			•	vable	Bion				vable	Biom				
Sorghum 0.0 2.8 4.0 1.3 4.0 5.0 6.8 9.7 6.8 9.7 12.4 11.4 12.9 11.4 12.9 Barley 0.7 0.0 4.7 2.8 4.7 3.1 5.0 7.2 5.0 7.2 7.7 8.3 9.6 8.3 9. Oats 0.1 0.7 1.2 0.7 1.2 1.3 1.8 2.5 1.8 2.5 3.2 3.0 3.3 3.0 3. Wheat (winter) 8.8 27.4 44.9 27.4 40.9 24.0 46.0 66.6 46.0 60.6 60.1 76.7 88.8 76.7 80. Wheat (winter) 2.2 7.4 12.2 7.4 10.9 8.0 15.7 22.7 15.7 20.3 20.1 26.2 30.3 26.2 27. (spring) 8.0 12.7 47.9 46.3 76.8 104.5 102.4 123.7		S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
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Oats	Sorghum	0.0	2.8	4.0	1.3	4.0	5.0	6.8	9.7	6.8	9.7	12.4	11.4	12.9	11.4	12.8
Wheat (winter) 8.8 27.4 44.9 27.4 40.9 24.0 46.0 66.6 46.0 60.6 60.1 76.7 88.8 76.7 80. Wheat (spring) 2.2 7.4 12.2 7.4 10.9 8.0 15.7 22.7 15.7 20.3 20.1 26.2 30.3 26.2 27. Soybean 0.0 0.0 10.0 12.7 47.9 46.3 76.8 104.5 102.4 123.7 115.8 128.0 139.3 170.6 164. Rice 0.0 10.3 14.7 10.3 14.7 5.7 10.3 14.7 10.4 14.7 14.2 17.1 19.6 17.1 19. Cotton 2.7 5.5 8.9 2.5 8.9 2.7 5.5 8.9 5.5 14.9 13.3 13.8 14.9 13.8 19. Other Crops 18.1 20.8 23.5 18.1 20.8 23.5 <	Barley	0.7	0.0	4.7	2.8	4.7	3.1	5.0	7.2	5.0	7.2	7.7	8.3	9.6	8.3	9.6
(winter) Wheat (spring) 2.2 7.4 12.2 7.4 10.9 8.0 15.7 22.7 15.7 20.3 20.1 26.2 30.3 26.2 27. (spring) Soybean 0.0 0.0 12.7 47.9 46.3 76.8 104.5 102.4 123.7 115.8 128.0 139.3 170.6 164. Rice 0.0 10.3 14.7 10.3 14.7 5.7 10.3 14.7 10.4 14.7 14.2 17.1 19.6 17.1 19. Cotton 2.7 5.5 8.9 5.5 8.9 2.7 5.5 8.9 5.5 14.9 13.3 13.8 14.9 13.8 19. Other 18.1 20.8 23.5 20.8 23.5 18.1 20.8 23.5 20.8 23.5 20.1 23.1 23.5 23.1 26. Crops 0.0 0.0 0.0 15.0 0.0 10.0 0.	Oats	0.1	0.7	1.2	0.7	1.2	1.3	1.8	2.5	1.8	2.5	3.2	3.0	3.3	3.0	3.3
(spring) Soybean 0.0 0.0 0.0 12.7 47.9 46.3 76.8 104.5 102.4 123.7 115.8 128.0 139.3 170.6 164. Rice 0.0 10.3 14.7 10.3 14.7 5.7 10.3 14.7 10.4 14.7 14.2 17.1 19.6 17.1 19. Cotton 2.7 5.5 8.9 5.5 8.9 2.7 5.5 8.9 5.5 14.9 13.3 13.8 14.9 13.8 19. Other Crops 18.1 20.8 23.5 20.8 23.5 20.8 23.5 20.1 23.1 23.5 23.1 26. Crops Double 0.0 0.0 10.0 15.0 0.0 10.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0<		8.8	27.4	44.9	27.4	40.9	24.0	46.0	66.6	46.0	60.6	60.1	76.7	88.8	76.7	80.8
Rice 0.0 10.3 14.7 10.3 14.7 5.7 10.3 14.7 10.4 14.7 14.2 17.1 19.6 17.1 19. Cotton 2.7 5.5 8.9 5.5 8.9 2.7 5.5 8.9 5.5 14.9 13.3 13.8 14.9 13.8 19. Other Crops 18.1 20.8 23.5 20.8 23.5 20.8 23.5 20.1 23.1 23.5 23.1 26. Crops Double Crop 0.0 0.0 10.0 10.0 0.0		2.2	7.4	12.2	7.4	10.9	8.0	15.7	22.7	15.7	20.3	20.1	26.2	30.3	26.2	27.1
Cotton 2.7 5.5 8.9 5.5 8.9 2.7 5.5 8.9 5.5 14.9 13.3 13.8 14.9 13.8 19. Other Crops 18.1 20.8 23.5 20.8 23.5 18.1 20.8 23.5 20.8 23.5 20.1 23.1 23.5 23.1 26. Crops 0.0 0.0 0.0 15.0 0.0 10.0 0.0 <t< td=""><td>Soybean</td><td>0.0</td><td>0.0</td><td>0.0</td><td>12.7</td><td>47.9</td><td>46.3</td><td>76.8</td><td>104.5</td><td>102.4</td><td>123.7</td><td>115.8</td><td>128.0</td><td>139.3</td><td>170.6</td><td>164.9</td></t<>	Soybean	0.0	0.0	0.0	12.7	47.9	46.3	76.8	104.5	102.4	123.7	115.8	128.0	139.3	170.6	164.9
Other Crops 18.1 20.8 23.5 20.8 23.5 18.1 20.8 23.5 20.8 23.5 20.1 23.1 23.5 23.1 26. Double crop 0.0 0.0 0.0 15.0 0.0 10.0 0.0 <t< td=""><td>Rice</td><td>0.0</td><td>10.3</td><td>14.7</td><td>10.3</td><td>14.7</td><td>5.7</td><td>10.3</td><td>14.7</td><td>10.4</td><td>14.7</td><td>14.2</td><td>17.1</td><td>19.6</td><td>17.1</td><td>19.6</td></t<>	Rice	0.0	10.3	14.7	10.3	14.7	5.7	10.3	14.7	10.4	14.7	14.2	17.1	19.6	17.1	19.6
Crops Double crop 0.0 0.0 10.0 15.0 0.0 10.0 0.0	Cotton	2.7	5.5	8.9	5.5	8.9	2.7	5.5	8.9	5.5	14.9	13.3	13.8	14.9	13.8	19.9
Crop Grasses (CRP) 0.0 0.0 15.4 15.4 0.0		18.1	20.8	23.5	20.8	23.5	18.1	20.8	23.5	20.8	23.5	20.1	23.1	23.5	23.1	26.1
(CRP) Trees		0.0	0.0	0.0	10.0	15.0	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(CRP) Wood 0.0 0.0 0.0 9.2 9.2 0.0 0.2 9.2 9.2 0.2 0.2 0.2 0.2 9.2 10. fiber Perennial 0.0 0.0 0.0 146.5 368.3 0.2 0.0 0.0 146.5 368.3 0.0 0.0 0.0 146.5 409. grasses		0.0	0.0	0.0	15.4	15.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
fiber Perennial 0.0 0.0 146.5 368.3 0.2 0.0 0.0 146.5 368.3 0.0 0.0 0.0 146.5 409. grasses		0.0	2.2	2.2	2.2	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
grasses		0.0	0.0	0.0	9.2	9.2	0.0	0.2	0.2	9.2	9.2	0.2	0.2	0.2	9.2	10.2
Total 107.4 246.8 372.4 441.9 822.9 204.4 386.8 542.3 558.0 936.4 492.1 620.9 718.1 819.0 1159.		0.0	0.0	0.0	146.5	368.3	0.2	0.0	0.0	146.5	368.3	0.0	0.0	0.0	146.5	409.2
	Total	107.4	246.8	372.4	441.9	822.9	204.4	386.8	542.3	558.0	936.4	492.1	620.9	718.1	819.0	1159.2

- S1 Current availability of biomass from agricultural lands.
- S2 Biomass from agricultural lands under moderate crop yield in crease without land use change.
- S3 Biomass from agricultural lands under high crop yield in crease without land use change.
- S4 Biomass from agricultural lands under moderate crop yield in crease with land use change.
- S5 Biomass from agricultural lands under high crop yield increases with land use change.

gross energy demand in the EU will be met using renewable energy in 2020, rising from a total of 85 million tons of oil equivalents (MTOE) in 2010 to 134 MTOE in 2020.²³ The estimation of EU biomass availability in 2012 was around 314 MTOE, expected to grow to 429 MTOE and then set at 411 MTOE in 2020 and 2030, respectively.²⁴ The different biomass resources that are available in EU are shown in Fig. 3(b).

The analysis of biomass availability shows that both in the EU and US the potential for the most sustainable biomass (i.e. wastes and residues), is considerable and represents the largest amount of the total. The EC defines residues as 'no land using crop', to indicate that their sustainable use ensures no additional pressure on land use. Nevertheless, it is always necessary to evaluate case by case the amount of residue that can be removed from the field without impoverishing the land. In the US, the potential for agricultural residues at 2030 is more than the double that of forest residues. In the EU, agricultural residues, wastes, and forestry residues also cover the largest share of the potential. Thus, from a sustainability point of view, the focus in the coming years will be on sustainably managed forestry, agricultural, and agro-industrial lignocellulosic residues, where the ILUC factor is less important than in the case of forestry/agricultural products.

The EU Intelligent Energy Biomass Futures project (www.biomassfutures.org) reported that the share of EU biodiesel on global demand will rise from 42% in 2010 to 74% in 2020, while bioethanol share will also rise to 13% in 2030. It must also be observed that meeting 2020 and 2030 EU biomass targets will require a significant import of feedstock from different parts of the world. Implications on direct and ILUC are currently under evaluation and discussion in Europe.

Biomass logistics

The bulk density of biomass is relatively low and occupies a larger volume compared to other solid materials used for energy such as corn grain or coal. As such, the bulk density significantly influences the transportation and storage of biofuel feedstocks, and becomes a major limiting factor with regard to the size of the biorefinery. A common estimate for feedstock consumption by the biorefinery is 2000 tons of lignocellulosic biomass/day or 7 to 8 million tons of biomass/year. In order to satisfy the biomass demand, yet limit transportation costs and associated GHG emissions, the transportation radius for the biorefinery is commonly set at 50 miles. Development of the biomass supply chain (harvest, collection, storage, preprocessing, handling, and

transportation) is of critical importance if lignocellulosic biofuels are ever to be successfully produced.

Biomass processing

Biomass has low bulk densities, 80-150 kg/m³ (for herbaceous) and 150-200 kg/m³ (woody biomass). Current biomass harvesting and bailing machinery produce either rectangular (130–200 kg/m³) or round bales (60–100 kg/m³). These materials should be densified to increase the bulk density and that will help in storage, loading, and transportation. A detailed study conducted by the Idaho National Laboratory (INL) transformed biomass bales into pellets (560-640 kg/m³ with 8-10% moisture) or briquettes (320-545 kg/m³ with 10-12% moisture) through a combination of milling and grinding followed by extrusion based densification. Binding agents (proteins or lignosulfonates) are usually used to hold biomass together. Pre-treatment processes (steam explosion, AFEX, and pre-heating) can relocate lignin to the biomass surface and improve the binding characteristics. Though there are several advantages of biomass densification, it comes with added capital for machinery/ energy cost (milling, briquetting, and cooling units) and requires additional safety measures including dust control systems and spark detection and fire protection systems.24,26

Biomass transportation and storage

For transportation purposes, both unit density (kg/m³) and bulk density (kg/m³) are important parameters. Biomass pellets and briquettes are preferred for biomass conversion due to high energy content per unit volume. Average pellet size (1/4 to 5/16 inches in diameter and up to 11/2 inch long) can be handled just like corn grain (45 lb/ft³) by truck and railroad, using the existing infrastructure.²⁷ On the other hand, special infrastructure is needed to handle and transport briquettes depending on their shape (pucks, logs of varying diameter and thickness). Moisture content of the biomass needs to be less than 10% moisture if they are to be stored for long periods of time without microbial degradation of biomass sugars. Another approach to reduce the biomass transportation and storage costs is to deploy Regional Biomass Processing Depots (RBPD) that can pre-treat and densify 100-200 tons of biomass per day that can then be transported to a centralized biorefinery. 28,29 Several thousand RBPDs can be set up around the country in a co-op fashion (involving several farmers) establishing a sustainable biomass supply chain.

Thermochemical and hybrid routes

The production of liquid and gaseous fuels from lignocellulosic feedstocks can also be carried out through thermochemical (or hybrid) approaches (Fig. 1). Thermochemical processes convert the organic matter into a mixture of liquid, gaseous, and solid products whose characteristics depend on the pre-treatment conditions, types of feedstocks, and downstream processing conditions.

In literature, the main biomass thermochemical conversion processes are often classified as torrefaction, (fast-intermediate-slow) pyrolysis, hydrothermal liquefaction and gasification. Torrefaction³⁰ is a biomass upgrading and energy-densifying pre-treatment step in which the lignocellulosic biomass is kept for sufficient time at temperatures between approximately 200 and 300 °C in the absence of oxygen. Biomass is thus converted into a hydrophobic product with an increased energy density and more favorable grind-ability (i.e. less energy is necessary to grind the biomass into small particles).

Pyrolysis³¹ is a process that decomposes biomass in the absence of oxygen at temperatures between 300 to 550-600 °C. Lower process temperatures and longer vapor residence times increase the production of charcoal, the pyrolysis solid product, while higher temperatures and longer residence times favor the gas phase production. Thus, depending on the process conditions (including the downstream steps such as vapor condensation), the relative amount of solid (char), liquid (pyrolysis oil) and gaseous products can vary considerably, as well as the pyrolysis oil properties. Also, the feedstock characteristics play an important role in the process. Fast pyrolysis maximizes the oil yield, a highly oxygenated acidic and viscous liquid, while slow pyrolysis, also named carbonization, has char is the main product. Both torrefaction and pyrolysis are more and more seen as possible pre-treatment steps before further conversion into liquid products or energy. In case of pyrolysis, it is also possible to upgrade the fuel through catalytic or hydro-de-oxygenation steps into a transport fuel.

Hydrothermal liquefaction is a thermochemical conversion process in which organic material is fed in a wet form to a high pressure (order of hundred bars) and temperature (typically $300-400\,^{\circ}$ C) reactor. The product contains less oxygen than pyrolysis oil and shows more favorable characteristics for downstream processing and use either as fuel or chemicals, but process conditions are very severe and represent a technological challenge.

Gasification occurs when, at higher temperature than pyrolysis or HTL, i.e. around 800–1500 °C or above), the

biomass is converted into a CO and $\rm H_2$ rich gaseous product. The producer gas composition depends on the reactor configuration, process conditions and gasification agent: different reactors should be chosen depending on the final destination. Depending on the final application, it can be necessary to convert the producer gas into a syngas fuel whose composition (e.g. $\rm H_2$ –CO ratio) is suitable for downstream processing (as FT reactions): this is always needed in the case of synthetic liquid production. The production of liquid fuels from biomass is possible based on the above mentioned processes.

Thermochemical conversion can effectively be used. For instance, catalytic reactors, as Fischer-Tropsch reactors, are used to convert a synthesis gas (syngas) consisting of a mixture of CO and $\rm H_2$ into hydrocarbons over a catalyst. Other possible process routes convert syngas to methanol, DME, hydrogen, and gasoline. Since, these are mostly catalytic processes, the removal of tar from syngas is a fundamental condition to allow proper operation and avoid catalyst poisoning.

Finally, regarding the hybrid process, some companies like Lanzatech and Coskata are first thermo chemically converting biomass to syngas via gasification and then converting them into liquid fuels by means of a microbial conversion process. Now several industrial initiatives, especially in the US, are testing this process route at demo scale. The other possible hybrid route includes companies like Byogy, CA, that converts ethanol produced using the biochemical route into jet fuel using a proprietary catalyst. Other companies, like Zeachem, produce acetic acid using fermentation route and hydrogenate them into ethanol using a catalytic route.

Biochemical and hybrid routes

Three different conversion scenarios are possible in a biorefinery (Fig. 1). They are:

- (i) Biological conversion, where biomass will be preprocessed by size reducing using milling, followed by chemical pre-treatment. Then, hydrolyzed to fermentable sugars both using acids or commercial enzymes and fermented to fuel molecules of different choices either using bacteria or yeast. In a few cases, the sugars producers are catalytically transformed to fuel molecules. Fuels molecules produced using fermentation or through a catalytic route are further distilled or separated to biofuels.
- (ii) Thermochemical conversion, where the processed biomass is either pyrolyzed to bio-oil/charcoal and

- catalytically upgraded to different fuel molecules or gasified to syngas/ash and processed through FT synthesis or microbial fermentation.
- (iii) Hybrid route, where fuels are chemically produced using a biological route and then further transformed by thermochemical/catalytic conversion (hybrid route) to another fuel molecule.

Biomass pre-treatment

In the biochemical conversion route, pre-treatment is one of the important processing steps, where different industries adopt different technologies. Pre-treatment can be classified into (i) physical pre-treatment (e.g. extrusion), (ii) chemical pre-treatment (e.g. using acid or base as a catalyst), (iii) physiochemical pre-treatment (e.g. wet oxidation, steam explosion), and (iv) biological pre-treatment (e.g. using microbes). Except for the biological pre-treatment process, which is time consuming, all are used in the industry. Several excellent review articles have been published in the past which provide more detailed information about these pre-treatment processes. ^{32–35} Some details about six well-established pre-treatment technologies that are used in the pilot plants in US and EU are given below.

Wet oxidation

Wet oxidation is an oxidative pre-treatment process where the biomass is wetted with water followed by passing oxygen/air (10-12 bar) at elevated temperatures (170–200 $^{\rm o}$ C). 36 Since this reaction is an exothermic reaction, the energy needed to heat up the reactor is relatively lower. Though this process solubilizes hemicellulose, most of them are present in an oligomeric form. Phenolic acids are the major degradation products produced during this pre-treatment, which are then degraded into other small organic acids like formic acid. Carbonates (Na₂CO₃) are usually added during the process, which elevate the pH to an alkaline condition. Several degradation products that are produced during wet oxidation are toxic for downstream processing. However, highly toxic compounds like hydroxyl methyl furfural (HMF) and furfural are produced in lower amounts. The high costs of carbonate and oxygen are the main bottleneck for this process.

Dilute acid

Cellulose present in biomass is more inert to acid when compared to hemicellulose and lignin. Almost 70–85% of hemicellulose in biomass could be solubilized depending on the pre-treatment conditions, which helps to hydrolyze

cellulose to glucose more efficiently when commercial enzymes are added. Acids are usually used either in dilute or concentrated forms. Companies like Virdia (Dansville, Virginia) use concentrated HCl (1-40%), as they have developed a patented process of efficient recovery and re-use of the catalyst. There is no need to add enzyme to hydrolyze the cellulose to monomeric sugars. However, the hydrolyzed sugars need to undergo a detoxification step prior to fermentation. Most other processes use dilute sulfuric acid (0.22-0.98%). Pre-treatment conditions include 140-180 °C, 15-60 minutes resident time. Most of the hemicellulose is hydrolyzed to xylose³⁷ which has to be either fermented separately or catalytically converted to other high value chemicals. Even at controlled conditions, xylose is further degraded into toxic inhibitory compounds like furfural. In addition to these compounds, several other phenolic degradation compounds are produced.³⁸ These degradation products have higher inhibitory effects when compared to alkaline pre-treatment processes and have a much lower inhibitory effect when compared to concentrated acids. NREL (Golden, CO) has pioneered this technology and has commissioned a pilot plant to study this process.

Steam explosion

This technology has been in existence since 1920, where it was used to make wood particle board. High pressure stream (280 °C, 1000 psi) was used in those processes. In a biorefinery process, biomass is subjected to a typical temperature range (160-260 °C) for several seconds and then discharged to a cyclone and collected in a different vessel.³⁹ During the pre-treatment, the fibers are mechanically disrupted, thereby increasing the surface area for easy enzyme access and producing a high sugar yield during hydrolysis. Several degradation products, like acetic, formic and levulinic acids, are produced in the process and are inhibitory to the microbes that are used in fermentation. Lignin melts at elevated temperatures and is re-polymerized and re-distributed to different parts of the plant cell wall. Recently dilute sulfuric acid or SO₂ impregnated hardwoods are used which reduces the pretreatment temperature and time to produce fewer degradation products.40

Ammonia based

Most of the alkali (KOH, NaOH, Ca(OH)) solvents available in the market are strong in nature and are soluble in water. Ammonia is a weak alkali and is volatile which provides an opportunity to recover and reuse it in the

pre-treatment process. It can be used as a gas, liquid ammonia 1 or as ammonium hydroxide. MBI and MSU together have developed a pre-treatment process called AFEX that uses either gaseous or anhydrous ammonia in the process. The pre-treatment is done at 100–140 °C using 1:1–3:1 ammonia to biomass ratio for a residence time (of 10–60 min). Only 3% of ammonia equivalent to biomass is consumed during pre-treatment, producing various nitrogenous compounds like amides (acetamide, feruloyl amide, cumaryl amide), and the remaining ammonia can recovered and reused. DuPont uses dilute ammonium hydroxide, which does not need an expensive recovery step. However, the residence time is longer and the process requires a neutralization step prior to hydrolysis and fermentation.

Mechanical extrusion

Almost all the pre-treatment processes required size reduced biomass. Size reduction includes chipping, milling (Hammer and knife) and grinding. Moisture content, rate of feeding and physical properties of biomass (hard wood or grasses) will influence the energy requirement for size reduction. For particle size reduction to 3-6 mm require about 11 kWh/ton of biomass (agricultural residues).42 However, switch grass, which has a higher silica content, requires about 30 kWh/ton, which corresponds to ~1% of the total energy content in biomass. For hard woods, size reduction to 0.2-0.6 mm requires require kWh/tonne and to 0.15-0.3 mm requires 100-200 kWh/ tonne. Other methods used for size reduction include mechanical extrusion process, 43 which helps to disrupt the biomass structure, causing defibrillation and reduced fiber length. Typical conditions used for this process include: screw speed 350 rpm, maximum barrel temperature 80 °C and in-barrel moisture content 40% (wet basis). Though this process is environmentally friendly when compared to thermochemical pre-treatment processes, dust pollution and high energy requirements are major concerns.

Hydrothermolysis/liquid hot water (LHW)

At super critical conditions (>320 °C), water loses its hydrogen bonding and becomes a weakly polar solvent that produces H⁺ and OH⁻ ions. When biomass is subjected to a super critical pre-treatment process, it gets solubilized and hydrolyzed. ⁴⁴ The high energy requirements needed for this process was one of the discouraging factors for this technology to become commercialized. However, some companies have started using this technology at pilot

scale with improved process development. Other researchers have demonstrated that LHW at controlled pH and milder conditions (190 $^{\rm o}$ C, 15 min) efficiently pre-treats biomass that could provide a 90% sugar yield using 15 FPU of enzymes. 45

Other pre-treatments

In addition to the above-mentioned well-established pre-treatment processes, other pre-treatments like lime, ionic liquids and organic solvents (e.g. ethanol) are also being used in commercial scale; their process details are reported elsewhere.³⁵ In particular, the successes of ionic liquid pre-treatment processes developed by companies like SuGanit and Hyrax (US) depend on the efficiency at which the ionic liquid can be recovered and re-used in the subsequent cycles due to high cost of catalyst.

After the biomass is subjected to pre-treatment using one of the above-mentioned process technologies, they undergo enzyme hydrolysis using commercial enzymes and are then subjected to microbial fermentation to produce biofuels. The details about the downstream processing steps are given below.

Enzyme Hydrolysis

For carrying out enzyme hydrolysis a commercial enzyme cocktail is used which consists of 40-50 enzymes with specific activities that are broadly classified into two classes of enzymes: (i) cellulase (that degrade cellulose) and (ii) hemicellulase (that degrade hemicellulose). 46 Companies like Novozyme, Genencore, Dyadic, DSM, and Iogen are commercial producers of these enzymes using different fungal strains. In the beginning, one cocktail of enzymes (comprising of cellululases and hemicellulases) was sold for hydrolyzing biomass. However, due to variation in the composition of the pre-treated biomass (e.g. dilute acid pre-treatment results is biomass comprising of higher cellulose content and lower hemicellulose content when compared to native feed stock, while ammonia pretreatment like AFEX does not change any composition after pre-treatment) the companies now sell two cocktails of enzymes to hydrolyze cellulose and hemicellulose. These enzymes can be mixed in different ratios depending on the feedstock composition. Most of the enzymes operate at 50 °C, while some of them originated from thermophile microbes and can operate between 60-65 °C. Many biofuel companies team up with enzyme producers to supply enzymes from centralized production facilities, or in some cases enzymes are produced on the site of a

biorefinery to overcome the cost issues (associated with concentrating the enzymes three-fold) and logistical issues (related to enzyme transportation cot). ⁴⁷ Cost of enzymes is one of the key factors that significantly influence the biofuel processing cost and companies are looking at innovative ideas to reduce the enzyme loading and recycle the enzymes over several batches of hydrolysis. After biomass is hydrolyzed into fermentable sugars it is fermented to different fuel molecules using microbes like bacteria or yeast, or in some cases chemically modified using catalysts.

Microbial fermentation

In some processes, the glucose and xylose stream are found together after hydrolysis (e.g. AFEX). While in others, the clean xylose sugar streams that are generated during pre-treatment (dilute acid or steam explosion) can either be combined with the glucose/xylose stream after hydrolysis or processed into chemicals using a biochemical or catalytic route. Separate hydrolysis and fermentation (SHF) is a time-consuming process (3–5 day hydrolysis and 3-day fermentation). However, SHF has some advantages: the microbes can be recycled for the subsequent fermentation cycles or can be processed and sold in the market as animal feed supplements. To overcome the processing time, simultaneous saccharification and co-fermentation (SSF/SSCF) is an option.⁴⁸ Here, the hydrolysis is kick-started at 50 °C for a period of 6 to 12 h. Then, the temperature is brought down to 30 °C and microbe seed cultures are added. Though the efficiency of enzymes (operating at low temperature) is sacrificed, there is some significant time savings. Also, there is some capital cost savings by performing hydrolysis and fermentation in one tank when compared to doing in two separate tanks. Some companies like Virent, Madison are catalytically converting these sugars into long chain alkanes (hybrid route). The process strategy of Mascoma Corporation is based on an innovative consolidated bioprocessing (CBP) approach. The CBP platform utilizes genetically modified yeast or bacteria to convert cellulosic biomass into bioethanol in a single step that combines enzyme production, enzymatic hydrolysis and fermentation.48

Biofuel processing

Biofuel processing is dependent on the type of biofuels produced in the industry. For example, in the case of ethanol (which is miscible in water) distillation is the

preferred option, followed by passage through molecular sieves (to remove residual water). In some cases perevaporation technology (separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane) is also followed. If the biofuel is immiscible in water (such as long chain alkanes and lipids), they separate out on the surface of the water and can be siphoned away. In the few cases where the biofuel produced is toxic to the microbes (e.g. butanol/iosbutanol), they are separated using affinity based separation techniques and further purified. In some cases (e.g. fatty alcohols) reactive distillation during fermentation is also used.

Comparing the Policy Framework in the EU and the US

After the current demonstration phase, the deployment of second-generation technologies in the EU and the US will probably move forward differently according to the Policy frameworks that is in place in each region. In the EU, major EU industries investing in the development of these processes and technologies clearly stated that:⁷ (i) secondgeneration advanced biofuel technologies are ready to compete with conventional biofuels, with EU companies keen to invest in commercial projects given appropriate conditions; and (ii) a stable long-term investment condition is needed, which will encourage investment while at the same time promote true advanced biofuels. This will have a positive economic as well as ecological impact on the EU. Other recent statements from the EU industry were given at the Third International Conference on Lignocellulosic Ethanol held in Madrid (June 2013).⁵⁰

Companies are asking for mandates for advanced biofuels, a clear growing pathway to 2030 and sustainability as reference criteria to evaluate any biofuel production. However, given the peculiarities of lignocellulosic fuels, certification schemes should also be further developed, harmonized among Member States and adapted to respond to the specific characteristics of lignocellulosic fuel chains, particularly when produced from agricultural and forestry residues and wastes (so-called 'no land-consuming feedstocks'). The current certification system in place in the EU is in fact very complex when applied to lignocellulosic residues from agriculture, and difficult to be implemented on an industrial scale on agricultural wastes.

Thus, the main concern from a technological and industrial point of view is the policy framework (including the agricultural policy) in place and its long term stability,

which is needed to secure investments and make projects become bankable in order to make them a reality. According to the EU industries, another urgent need is the development of suitable financing schemes to cover risks and provide guarantees for these very innovative technologies. The situation in the US (and Brazil, even if not discussed here) looks instead very different, with the industrial activities on advanced biofuels and biorefineries supported by the DOE (and BNDES, in Brazil) not only through various forms of grants but also risk covering measures. A number of demo plants are being built in the US, as reported in this work, as the proposed projects gets implemented, conditions could be even more favorable for further commercialization and large scale deployment.

As of today, the EU is in a well-advanced stage of technology development when compared to the US. Given the existing policy framework in the US, it is most likely that the commercial deployment of advanced biofuel generation technology will take place at a faster rate in the US, if no specific measures are taken in Europe. The result of this unclear policy and financial framework is that the EU industries, leading today the technological global competition on advanced biofuels, after having developed their demo plant in the EU, will invest abroad due to less complex and more stable and favorable conditions. This is the case of M&G, partnering with Graalbio in Brazil, where a plant similar to the demo plant in Crescentino is already under construction and new ones will follow, or Abengoa, which is constructing a large industrial demo plant in Hugoton (KS), USA.

Conclusion

A complete summary of biofuels demonstration and commercialization activity in the US and in the EU are presented in this review. A majority of the projects in the US and the EU are either at pilot/demonstration scale or under advance stages of construction of commercial plants. Presently, bioethanol via a biochemical route is the leading process strategy in the US and in EU. The US EISA, 2007 mandates 36 billion gallons of advanced biofuels production per year by 2022 from non-cornstarch-based biomass (sugars or cellulose); whereas the EU's initiative is guided by its 2007 climate and energy 20-20-20 targets with 10% contribution of renewable fuels in transport. With respect to biomass availability, it is projected that about 1.3 billion tons of lignocellulosic biomass per year can be available in the US to meet the advanced biofuels objectives. The biomass resources in the EU may not be adequate for meeting the 2020 and 2030 EU biofuels targets and it may require a significant import of biomass feedstock from different parts of the world. In view of upcoming processing strategies, thermochemical and hybrid routes provide potential to produce 'drop in' biofuels that are compatible with the existing transportation infrastructure.

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Disclaimer

Authors presented data collected through review of available literature, analysis of publications, press and personal contacts. Information here given is to the best of their knowledge, but not necessarily totally exhaustive, complete, or updated. Some deviations from factual situation may be presented. The presentation does not claim to completely cover the given topic.

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Dr Venkatesh Balan

Dr Venkatesh Balan has been an Associate professor at Department of Chemical Engineering and Material Science, Michigan State University since July 2009. He is associated with Great Lakes Bioenergy Center research (one of the three energy center established by the US Department of Energy)

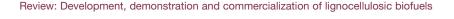
activities since it was established in 2007. Currently his research is concentrated in the areas of biomass pretreatment, enzyme hydrolysis, microbial fermentation, and extraction of protein from biomass. Some of his present projects include, understand the pre-treatment conditions using ammonia, surface properties of biomass after pretreatment, high through put hydrolysis and sugar analysis using micro plate assay, how the Saccharified biomass can be fermented to fuels/chemicals and valorize lignin for fuel and material applications. Dr Balan is a biophysical chemist by training has more than 20 years of experience working in both industry and universities in the areas of protein expression, protein engineering and using proteins for various useful applications.



Dr David Chiaramonti

Dr. David Chiaramonti eaches Bioenergy Conversion Technologies at the University of Florence, School of Engineering. He is member of CREAR and chairman of the Renewable Energy Consortium for R&D (RE-CORD), University of Florence. His main scientific interest is on the production and use of biofuels,

either liquid, gaseous or solid. His research work covers thermochemical biomass conversion processes (torrefaction, pyrolysis and gasification) as well as liquid biofuel production, upgrading and use. Some of the recent activities deal with aviation biofuel production, catalytic pyrolysis and gasification of biomass in pilot/demo reactors, algae cultivation systems and methanation. He is author of more than 130 publications on International Journals and Conferences, and participated to more than 25 EU R&D and dissemination projects, in particular in the field of Biomass. Formerly member of IEA-Bioenergy, Task 34, Biomass Pyrolysis, since 2010 he joined IEA Task 39 (Liquid Biofuel) as Country Representative. He is a member of several associations and scientific committees, as ISAF (Int.Symposium on Alcohol Fuels), ICAE, the Italian and the European Biofuel Technology Platforms, and ISES-Italia.





Dr Sandeep Kumar

Dr Sandeep Kumar is currently an Assistant Professor in the Department of Civil and Environmental Engineering at Old Dominion University, Virginia, USA. He earned his PhD in Chemical Engineering from Auburn University, USA in 2010. Dr Kumar's research focuses on the application of sub- and supercritical water technology for the conversion of lignocellulosic biomass/algae to advanced biofuels. His research interests are in the area of pre-treatment (for bioethanol), liquefaction (for biocrude/bio-oil), carbonization (for biochar/biocoal), and gasification (for syngas, methane, and hydrogen) of non-

food based biomass. Dr Kumar's expertise is in high temperature and high pressure hydrothermal reactions involving biomass components such as proteins, lipids, cellulose, hemicelluloses, and lignin. He has more

than 15 years of experience in industry and R&D (biofuels, carbon black, and nuclear fuels) with responsibilities in new process development, process engineering and project management.