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A new perspective in bio-refining: levoglucosenone and cleaner lignin from waste biorefinery hydrolysis lignin by selective conversion of residual saccharides.

M. De bruyn<sup>a</sup>, J. Fan<sup>a</sup>, V. L. Budarin<sup>a</sup>, D. J. Macquarrie<sup>a</sup>, L. D. Gomez<sup>b</sup>, R. Simister<sup>b</sup>, T. J. Farmer<sup>a</sup>, W. D. Raverty<sup>c</sup>, S. J. McQueen-Mason<sup>b</sup>, J. H. Clark<sup>a,\*</sup>

<sup>a</sup> The Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, United Kingdom

<sup>b</sup> The Centre for Novel Agricultural Products, Department of Biology, University of York, York, YO10 5DD, United Kingdom

<sup>c</sup> Department of Chemical Engineering, Monash University, Clayton, Victoria, 3800, Australia

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# **Materials**

Waste hydrolysis lignin was kindly received from SEKAB (Processum Biorefinery, Sweden). This was the result of applying SEKAB's E-tech process to milled softwood.

Hydrolysis lignin of the type used in this investigation can be produced by the following procedure that is typical of many used in cellulose to ethanol plants:

Spruce sawdust was pre-treated by taking spruce sawdust (1,000 kg, 0.1 - 3 mm) particle size and mixing it with 0.051 M aqueous sulfuric acid (3,000 L) and passing this mixture through a heated screw pressure reactor at 190 °C with a residence time of 180 seconds. The pre-treated sawdust suspension was discharged from the reactor directly into a flash tank equipped with a heat exchanger where the steam flashing off at atmospheric pressure carried away most of the volatile inhibitory compounds, such as pine terpenes and furfural. The residual suspension was pumped to a tank containing 25,200 L 0.012 M aqueous sodium hydroxide equipped with an efficient mechanical stirrer. The suspension was pumped through a series of tubular heat exchangers to adjust the temperature of the suspension to 45 °C. The suspension was pumped into a 50 cubic metre batch fermenter equipped with cooling coils and the pH was adjusted to pH 5.0 by addition of 4M sodium hydroxide solution. Diammonium hydrogen phosphate (2.35 kg) was dissolved in the suspension and cellulase (5.6 kg CTec2, Novozymes A/S) and xylanase (0.6 kg HTec2, Novozymes A/S) enzymes mixed with an inoculum of Saccharomyces cervisiae Strain BY4742 were added to the suspension. Stirring was continued for 96 hours while the temperature of the broth was maintained at 45 - 50 °C. At the end of the incubation period the suspension was pumped onto a belt press and filtered to remove solid particulate waste hydrolysis lignin and the filtrate was collected and pumped to a falling film evaporator for extraction of ethanol.

# **Experimental method**

Crude waste softwood-derived hydrolysis lignin (CSHL) (1.4 g) was placed into a 10 mL vial and heated using microwaves (250 W) in a CEM 'Discover' MW generator, to 180

°C. This typically required less than 5 min. The softwood hydrolysis lignin contains residual saccharides [~20% of dry weight (DW)], 59.5% water, and ~2% residual sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Steam formed in the process, whether coming from water already present in the mixture or from water formed by dehydration of saccharides, was allowed to escape from the reaction mixture. This typically occurs in between 90-140°C. The aqueous mixture is prevented from returning to the reaction mixture and comprises, as determined by GC-MS analysis, acetic acid and furfural. When the target temperature of 180°C was reached, the reactor was cooled to room temperature. The resulting material was extracted multiple times with acetone to extract the levoglucosenone formed in the process. The acetone was removed using a Rotavap (vacuum) at room temperature in order to isolate the crude levoglucosenone.

On one occasion several runs of this reaction were made as to obtain a sizeable amount of levoglucosenone, proving the concept:

Run A; sample weight: 1.4054g - temperature of 173°C reached after 3,5 min Weight 'glass flask + product' before: 19.569g Weight 'glass flask + product' before: 18.972g Mass loss = 19.569g - 18.972g = 0.597g

Run B; sample weight: 1.4079g - temperature of  $173^{\circ}C$  reached after 4,5 min Weight 'glass flask + product' before: 19.721gWeight 'glass flask + product' before: 19.077gMass loss = 19.721g - 19.077g = 0.644g

Run C; sample weight: 1.408g - temperature of  $180^{\circ}$ C reached after 4 min Weight 'glass flask + product' before: 19.742gWeight 'glass flask + product' before: 19.172gMass loss = 19.742g - 19.172g = 0.57g

Run D; sample weight: 1.403g - temperature of 180°C reached after 4 min Weight 'glass flask + product' before: 19.753g Weight 'glass flask + product' before: 19.229g Mass loss = 19.753g - 19.229g = 0.524g

Run E; sample weight: 1.4011g - temperature of 180°C reached after 4 min Weight 'glass flask + product' before: 19.578g Weight 'glass flask + product' before: 19.085g Mass loss = 19.578g - 19.085g = 0.493g Run F; sample weight: 1.414g - temperature of 180°C reached after 10 min

Weight 'glass flask + product' before: 19.680g

Weight 'glass flask + product' before: 19.10g

Mass loss = 19.680g - 19.10g = 0.580g

Run G; sample weight: 1.4109g - plateau temperature of 180°C reached after 4 min

Weight 'glass flask + product' before: 19.653g

Weight 'glass flask + product' before: 19.047g

 $Mass \ loss = 19.653g - 19.047g = 0.606g$ 

Run H; sample weight: 1.424g - plateau temperature of 179°C reached after 4,5 min

Weight 'glass flask + product' before: 19.700g

Weight 'glass flask + product' before: 19.162g

 $Mass \ loss = 19.700g - 19.162g = 0.538g$ 

Run I; sample weight: 1.423g - plateau temperature of 180°C reached after 3,5 min

Weight 'glass flask + product' before: 19.567g

Weight 'glass flask + product' before: 19.034g

Mass loss = 19.567g - 19.034g = 0.533g



# **CHN** analysis

Material	%C	%H	%N	%rest
Dry CSHL	53.78	5.9	0	40.32
Recovered lignin	59.40	5.33	0	35.27

# Analysis

## GC-MS

The acetone extract of the microwave heated CSHL was analyzed on a Waters GCT Premier TOF mass spectrometer coupled to an Agilent Technologies 6890A gas chromatograph equipped with a 30 m x 0.25 x 0.25 ZB-5HT inferno column. The MS acquisition mass range was between m/z 50 and 750, electron energy 70 eV, trap current 200 uA. The GC method used was isothermal for 1min at 60 °C and then an increase to 350 °C at 15 °C/min, hold for 9.67 mins at maximum temperature, total runtime 30 mins.

## NMR

Qualitative <sup>13</sup>C NMR spectra were recorded on a Jeol ECX-400 spectrometer at 100MHz. The central resonance of CDCl<sub>3</sub> ( $\delta$ C = 77.23 ppm) was used as the internal reference.

# FT-IR

FT-IR analysis of samples was carried out on a Bruker Vertex 70 instrument equipped with "Specac" Golden Gate Single Reflection Diamond ATR accessories. For recording samples 64 scans at 2 cm<sup>-1</sup> resolution was used.

## XPS

XPS spectra were recorded on a Kratos Axis Ultra DLD photoelectron spectrometer using a hemispherical photoelectron analyser with a monochromatic AlK $\alpha$  X-ray source (75– 150 W) and analyser pass energies of 160 eV (for survey scans) and 40 eV (for detailed scans). Samples were mounted using double-sided tape. Binding energies were referenced to the C 1 s binding energy 285 eV. Prior to analysis samples were degassed overnight at ultrahigh vacuum (<5×10<sup>-10</sup> Torr). CasaXPS software was used to carry out analysis of the spectra.

### SEM

SEM micrographs were recorded using a JEOL JSM-6490LV. Samples were mounted on alumina plates and coated with a 7 nm layer of Au/Pd using a high resolution sputter SC-7640 coating device prior to analysis.

## N<sub>2</sub> adsorption

The residual washed lignin was analyzed by  $N_2$  adsorption/desorption on Micromeritics TriStar porosimeter. BET model was applied for surface area determination, BJH model applied for total pore volume determination (mesopore and micropore volume) and t-plot for micropore volume determination.

#### Mono- and oligosaccharide analysis

Oligosaccharide analyses of the sugars released from hydrolysis lignin was performed by aqueous extraction of the lignins. The samples were filtered using a Millex LH 0.45  $\mu$ m pored filter (Millipore, Billerica, USA) and then separated by high-performance anion-exchange chromatography (HPAEC) on a Dionex Carbopac PA-20 column with integrated amperometry detection. The separated oligosaccharides were quantified by using external calibration with an equimolar mixture of eleven monosaccharide and oligosaccharide standards (glucose, cellobiose, cellotriose, cellotetraose, cellopentaose, cellohexaose, xylose, xylotriose, xylotetraose, and xylopentaose).

Monosacharides were analysed using the same method, but the dried samples were hydrolysed with 2 M trifluoroacetic acid at 100°C for 4 h. After the acid was evaporated, samples were rinsed with isopropanol and re-suspended in 100  $\mu$ L of deionised water. Samples were filtered and analysed as described above. The monosaccharide standards used for quantification were arabinose, fucose, galactose, galacturonic acid, glucose, glucuronic acid, mannose, rhamnose, and xylose.

## **ICP-MS** analysis

Inductively Coupled Plasma (ICP) was carried out to measure the sulphur concentration in solution using an Agilent 7700x fitted with a standard Ni sample and skimmer cones and coupled to a Mass Spectrometer (MS). The samples were run in No Gas mode.

- a) Microwave Digestion: 0.3142 g of hydrolysis lignin digested using 8 mL of 69% nitric acid + 2 mL H<sub>2</sub>O<sub>2</sub> + 90 mL water; Microwave details: 200 °C (ramp time 40 min), hold time: 15 min, cooling using airflow.
- b) 1:10 dilution before ICP-MS analysis
- c) Every sample was run in triplicate to ensure that a standard deviation could be calculated

Sample 1: 2453089.43 ppb [RSD: 6.3]

Sample 2: 2742183.91 ppb [RSD: 5.6]

Sample 3: 2536744.91 ppb [RSD: 5.4]

Average of the three samples (essentially nine samples): 25773394.17 ppb = 2577.3394ppm = 2577.3394 mg S / kg (wet hydrolysis lignin) (internal direct recalculation in the software rather than mg S / liter).

This equals 0.257 wt% S – and corrected for the water content in the hydrolysis lignin of 59.5% this makes 0.634 wt% S. This is equivalent to 1.94 wt%  $H_2SO_4$ .

# Quantitative TG-IR and its quantitative use determining conventional thermal levoglucosenone formation

# TG-IR

TG-IR experiments were performed using a Netzsch STA 409 cell and TASC 414/3 controller attached to a Bruker Equinox 55 spectrophotometer and typically using 50-100 mg of sample. The thermograms were recorded using a heating rate of 10 K min<sup>-1</sup> from room temperature till 1173 K and using a flow rate of the N<sub>2</sub> carrier gas of 100 cm<sup>3</sup> min<sup>-1</sup>. Every 20 s an infrared spectrum in the region 400–4000 cm<sup>-1</sup> of the evolved fragments from the carbonaceous materials was recorded. The FT-IR spectra were recorded on an FT-IR spectrometer from Bruker Analytik.



Figure 1S: TG-IR spectra of hydrolysis lignin and reference compounds

Regarding the quantitative processing of FT-IR spectral data it has been previously shown by Bassilakis et al. that a combined TG-(FT-IR) method can be effectively applied to the quantitative analysis of volatile pyrolysis products.<sup>1</sup> In the present work, the quantitative analysis of levoglucosenone (formed under conventional thermal heating) was performed using the OPUS (OPtical User Software)/CHROME software package (OPUS 5.0 software) from Bruker Analytik.

Using a specific OPUS procedure this allows for the estimation of the amount of levoglucosenone formed during the thermal pyrolysis of hydrolysis lignin.

The FT-IR spectra were firstly analysed for the occurrence of levoglucosenone as a function of temperature. The spectrum of levoglucosenone was found to be clearly identifiable as shown convincingly in Figure 1S and this permits quantitative analysis. This was effectively the case around 310 °C (583 K) where a still complex FT-IR spectrum occurs (see Figure 1S bottom spectrum) yet with all the characteristic levoglucosenone peaks being 2994, 2897, 1734, 1105, 991, 903 and 827 cm<sup>-1</sup> clearly visible (reference levoglucosenone IR spectrum given in green). At that stage also some HMF, formic acid and formaldehyde are identifiable. All these spectra are clearly displayed in Figure 1S.

Secondly, the TGA of pure levoglucosenone (45.6 mg) was recorded showing that 87% can be effectively vaporized with a maximum vaporization rate at ~189 °C (462 K), and thus more specifically 45.6 mg \* 0.87 = 39.67 mg of effective levoglucosenone evaporation is observed. This is shown in Figure 2S.



Figure 2S. TGA analysis of the hydrolytic lignin

Thirdly, a TG-IR experiment using pure levoglucosenone permitted a correlation to be made between the mass loss and the cumulative IR intensity of the levoglucosenone spectrum. The cumulative IR intensity of levoglucosenone was estimated as the area below the kinetic trace of levoglucosenone evaporation. This kinetic trace is derived from all the FT-IR spectra obtained during the experiment (Figure 3S). Each point of this trace represents the levoglucosenone content in the vapour phase.



Figure 3S. Kinetic trace of pure levoglucosenone evaporation.

In cases where a gaseous mixture is present, resulting for example from the pyrolysis of hydrolysis lignin, then the curve measures the content of levoglucosenone in this mixture using a standard OPUS linear regression procedure. With the maximum gaseous levoglucosenone content at 1290 s (i.e. 189 °C) normalized to 1, the cumulative IR intensity of the levoglucosenone was found to be 446.3 s. (A.U. x s) So a unit area represents 39.67 mg/446.3 s = 0.08888 mg/s



Figure 4S. Kinetic trace of levoglucosenone produced during pyrolysis of the hydrolysis lignin.

Figure 4S shows the kinetic trace of levoglucosenone produced during the pyrolysis of hydrolysis lignin (88.1 mg). With the area under the curve being 60.1 s, the total amount of levoglucosenone formed during the pyrolysis of hydrolysis lignin can then be estimated as: 0.08888 mg/s x 60.1 s = 5.34 mg. This represents 6.06 % of the original dry lignin mass.





Figure 5S. GC-MS of an acetone extract of the hydrolysis lignin

# Figure 6S: Determination of residual acidity by leaching and titration



Figure 6S. acid leaching/titration of nine consecutive water washes of the CSHL



Figure 7S: Pyrolysis experiment (250 W until 180 °C) on water washed CSHL

**Figure 7S.** Pyrolysis experiment of water washed hydrolysis lignin to 180 °C (250 W) and analyzed by <sup>13</sup>C NMR (acetone-d6).

Figures 8S and 9S: DSC traces of original and washed hydrolysis lignin – and as a reference also Sigma-Aldrich reagent grade lignin



Figure 8S. DSC traces of ref. Sigma-Aldrich reagent grade lignin and original/washed hydrolysis lignin



# Zoomed in DSC traces of original and washed hydrolysis lignin

The thermal event around 180 °C has disappeared after washing and only a very small thermal event around 200 °C is noticeable

**Figure 9S.** Expansion of the relevant sections highlighted in Figure 6S of DSC traces of original and washed hydrolysis lignin

# Figure 10S: Scheme of the experimental microwave set-up



Figure 9S. scheme of the experimental microwave set-up

 Table 1S: overview of a range of methods and a range of conditions to synthesize levoglucosenone

	Raw	Т	LGE	LGE	Catalyst	Additive	Heating	Ref.
	material	(°C)	yield	selectivity	, i		method	
1		350	2.4 wt%					
			(3.1					
			mol%)					
2		300	8.9 wt%		Phosphoric acid			
			(11.5		3wt%			
			mol%)					
3		250	19 wt%					
	Cellulose		(24.4					
			mol%)			-	Conventional	2
4		300	21.4 wt%			[BMMIM]		
			(27.6			CF <sub>3</sub> SO <sub>3</sub>		
_		250	mol%)			(50 wt%)		
5		350	22.0 wt%			, , ,		
			(28.9)					
6		200	11101%)					
0	Levogluc	300	0.3  W1%					
	osan		(0.3)					
7		200	29.9 mol%		Sulphuric acid 0.1			
8		240	36.2 mol%		wt%		Conventional	3
9		280	33.4 mol%					
10		200	4.9 mol%		Sulphuric acid 1			
11		240	1.7 mol%		wt%			
12		240	25.4 mol%		Polyphosphoric	Sulfolane		
13		280	22.3 mol%		acid 0.1 wt%			
14	Cellulose	240	36.2 mol%		Polyphosphoric			
15		280	38 mol%		acid 1 wt%			
16		240	30.6 mol%		Polyphosphoric			
					acid 5 wt%			
17		200	42.2 mol%		Sulphuric acid 0.1	Sulfolane		
					wt%	+ 0.1 atm		
						vacuum		
18	Cellulose	270	3-5% yield		Phosphoric acid		Conventional	4
19	Centulose		6.61%		Thosphone dela		MW (620W)	-
20	Microcry	270	3.79%	13.67%	-			
21	stalline	290	5.84%	16.32%	Sulfuric acid		-	
22	cellulose	320	5.17%	11.74%	0.05M			
23	Bagasse	270	7.58%	20.99%			-	
24		270	5.53%	13.19%	Phosphoric acid			_
~ ~		200	< 1 <b>2</b> 0/	10.000/	3%		Conventional	5
25	Bagasse	290	6.12%	13.82%			-	
26		320	0.20%	12.39%			1	
21		330	3.04%	9.09%			4	
28	Bagasse	290	3.4/%		Phosphoric acid		4	
29	-	320 250	3.34% 0.60%		J%			
30	Microcry	230	0.09%	23%			Conventional	6

31	stalline	350	3.8%	10%				
	cellulose	100						
32		400	5.4%	1%				
33	$H_3PO_4$	250	4.35%	87%	Phosphoric acid			
34	treated cellulose	300	6.09%	87%	treated cellulose			
35	Microcry	300	1.75%	7%				
36	stalline cellulose	300	4.96	16%	MCM-48			
37	H <sub>3</sub> PO <sub>4</sub> treated	300	11.4%	95%	AlFe-MCM-48 (high acidity catalyst!)			
38	centulose	350	9.6%	96%	MCM-48			
39	Mianaamu	250	6.39%	71%				
40	where	250	1.83%	61%				
41	cellulose	250	0.98%	49%	Nb <sub>2</sub> O <sub>5</sub> (high acidity catalyst!)		MW	
42	H <sub>3</sub> PO <sub>4</sub> treated cellulose	250	3.08%	77%	Phosphoric acid treated cellulose			
43	Cellulose	300	15.43wt%		$SO^{2}/TO$ Fo O	Feedstock/		
44	Poplar wood	300	7.06wt%		(magnetic superacid)	catalyst ratio of 1:1	Conventional	7
45	Cellulose	300	29.7wt% (38.2 mol%)			[EMIM]C H <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO 3	Conventional	8
46		190	43	84%	20mM Sulphuric	THF	Conventional	9
47	Cellulose	210	51	89%	acid in THF			
48		230	47wt%	88%				

1 Bassilakis, R; Carangelo, R.M.; Wojtowicz, M.A. Fuel , **2001**, 80 (12), 1765-1786

2. Kudo, S.; Zhou, Z.; Norinaga, K.; Hayashi, J.-i. *Green Chemistry* **2011**, 13, (11), 3306-3311.

3. Kawamoto, H.; Saito, S.; Hatanaka, W.; Saka, S. *Journal of Wood Science* **2007**, 53, (2), 127-133.

4. Sarotti, A. M.; Spanevello, R. A.; Suarez, A. G. *Green Chemistry* **2007**, 9, (10), 1137-1140.

5. Sui, X.-w.; Wang, Z.; Liao, B.; Zhang, Y.; Guo, Q.-x. *Bioresource Technology* **2012**, 103, (1), 466-469.

6. Luz Nieva, M.; Alicia Volpe, M.; Laura Moyano, E. *Cellulose* **2015**, 22, (1), 215-228.

7. Lu, Q.; Ye, X.-n.; Zhang, Z.-b.; Dong, C.-q.; Zhang, Y. *Bioresource Technology* **2014**, 171, 10-15.

8. Kudo, S.; Zhou, Z.; Yamasaki, K.; Norinaga, K.; Hayashi, J.-i. *Catalysts* **2013**, 3, (4), 757-773.

9. Cao, F.; Schwartz, T.; McClelland, D.; Krishna, S.; Dumesic, J.; Huber, G. *Energy & Environmental Science* **2015**, 8, 1808-1815

# Notes on Industrial Relevance of Microwaves

Informative list of the key-lectures at the AMPERE (Association for Microwave Power in Europe for Research and Education) 2015 conference, <u>in the industrial sessions</u>, in September 2015:

- Microwave baking of bread and bakery products possibilities for energy reduction [B. Raaholt]
- The microwave cooking and drying of muesli an operating industrial application [R. Schiffmann]
- Microwave-driven plasma gasification for biomass waste treatment [Prof. Georgios Stefanidis]
- Design of a lab-scale high pressure microwave flow reactor for raw oil treatment [A. Rosin, M. Willert-Porada and collaborators]
- Application of radio frequency heating as a post drying step in apple chip production [T.K. Palazoglu]
- Keynote lecture by Prof. K. Huang: Microwave Power Applications in China: an overview was given of the current use of microwave technology in the Chinese industry. The message was crystal clear in that more than 120 Chinese companies are currently operating processes using radio frequent heating some illustrative examples being: 1) lignite drying and desulfurization 2) treatment of hazardous waste 3) mineral drying 4) microwave dryer of green tea (60kW!) 5) rubber vulcanization 6) the making of activated carbon from bamboo using a 400kW (!) 915 MHz (!) microwave device 6) regeneration of activated carbon 7) medicinal herb drying 8) ceramic forming 8) multiple 10-50 kW (!) microwave reactors operating at 2.45 GHz for industrial chemical syntheses.
- Microwave processing of high entropy alloys: a powder metallurgy approach [M. Garuti: the co-founder and president of Alter Power Systems now MKS instruments]
- Dipolar absorption of electrical energy [S. Lefeuvre]
- Thermal cracking of lignite briquettes for gasification in pressurized reactors with a 10 kW microwave applicator [M. Zink]
- Dielectric properties of sugarcane at different temperatures and concentrations using a continuous measurement device [M.I. Berto]
- Microwave technology for efficient curing of fibre composites, an overview about the FLAME project [J. Jelonnek]
- An innovative set-up for impedance matching a TM010 waveguide resonator a field report from industry [M.J. Kammerl]
- Principles of design for industrial microwave applicators [J. Jelonnek]

# Upscaling and industrial relevance of the described microwave process

One of the authors (Dr. Warwick Raverty) is prime chemistry consultant to the Australian company Circa Group who with Circa senior management has advised on commercial LGE production and technology scalability of this process.

The Circa Furacell<sup>2</sup> process produces LGE from the acid-catalyzed pyrolysis of pine sawdust. This is now being upscaled in a \$6.5 million large-scale prototype plant in collaboration with Norske Skog. This demonstrates clearly that pyrolysis can be a realistic and viable larger scale process for the making of LGE.

In relation to LGE production from (ligno)cellulose, the publications by Shafizadeh<sup>3</sup> in the early seventies reported that 8 mol% of levoglucosenone yield could be achieved on a 1g scale but that only 2 mol% levoglucosenone yield could be achieved at 20g scale. Using continuous vacuum flash pyrolysis it was shown that it is indeed possible to obtain levoglucosenone in larger scale (Circa patent<sup>1</sup>). LGE is a stable chiral molecule that can be distilled under vacuum - *in marked contrast to its thermally unstable and achiral isomer HMF*. Circa have obtained a 20% higher LGE yield than reported by Shafizadeh demonstrating the importance of carefully designed large scale processing equipment that provides minimal contact of levoglucosenone vapours with hot cellulose char and rapid removal from the pyrolysis zone. Circa assess the discovery reported here of particular importance as it shows a straightforward way to produce LGE at atmospheric pressure in air. It is believed that the method will be easily scalable using existing commercial scale microwave tunnel heating technology (for instance equipped with a conveyor belt or screws) of the type used to dry fruits and vegetables. A good measure of their confidence is that Circa and the University of York have jointly applied for patent protection prior to submitting this manuscript for publication.

With regard to the condensation of LGE, the current pilot plant removes the compound from (cellulosic) biomass by vacuum distillation and we would envisage the same technique being used in the scale-up of our process.

<sup>&</sup>lt;sup>2</sup> Court, G. R. H. S., East Melbourne, Victoria 3002, Au), Lawrence, Christopher Howard (79 Smiths Road, Templestowe, Victoria 3106, Au), Raverty, Warwick Douglas (8 Bannockburn Road, Viewbank, Victoria 3084, Au), Duncan, Anthony James (20 Hammond Street, Brighton, Victoria 3186, Au) Method For Converting Lignocellulosic Materials Into Useful Chemicals. Wo/2011/000030, 2011.

<sup>&</sup>lt;sup>3</sup> Shafizadeh, F., Furneaux, R. H. and Stevenson, T. T., *Carbohydrate Res.*, (1979) **71**, 169-191

# In depth discussion applications of LGE/Cyrene<sup>TM</sup>

# • Use of LGE for fine chemistry

We agree with the reviewer that until recently the market for LGE was small and the price very high. One development of broadleaf herbicides by ICI Agrichemicals (UK) failed due to the non-availability of tonne quantities of LGE.<sup>4</sup> In very general terms scalable production of chiral LGE at commercially attractive prices will allow revisiting these and other fine chemical opportunities.

Recently Allais et al.<sup>5</sup> showed (and patented<sup>6</sup>) that it is possible to obtain (S)- $\gamma$ -hydroxymethyl- $\alpha$ , $\beta$ butenolide (HBO) and (S)-y-hydroxymethyl-y-butyrolactone (2H-HBO) from LGE or dihydro-LGE (Cyrene) through enzyme mediated Baeyer-Villiger oxidation. Thereby HBO is of particular interest for the pharmaceutical industry as many drugs (e.g. Burseran or Isostegane) and antiviral agents against HIV or hepatitis B can be efficiently synthesized from it. On the other side 2H-HBO can serve as the starting point for a range of so-called C7 to C12 5-alkyl- and 5-alkenyl-γ-lactones. These compounds occur naturally in a range of fruits, nuts and even dairy products at part per million levels and they contribute in a major way to the flavour of these foods. In particular (S)-5-[(Z)-Oct-2-en-1yl]tetrahydrofuran-2-one (ZOTO) occurs in milk, butter, cheeses and other dairy products and an increased concentration of this material in these products has been shown to have a major influence on the flavour rating of the dairy product. ZOTO, with unspecified enantiomeric purity, has become an article of commerce under the trade name 'dairy lactone', however it is available in very limited quantities and is thus currently far too expensive to be used in manufacture for all but the highest value dairy products. The dairy industry has a major adverse environmental impact on many regions of the world because of its high per kilogram usage of fresh water in processing dairy products. Production of products based on so-called 'soy milk' consume far lower quantities of fresh water, yet are rejected by many human consumers because they perceive the soy flavour as distinctly different to that of dairy. Potential production of ZOTO from LGE and/or Cyrene at much lower cost, and its introduction to soy-based products as a nature-identical dairy flavouring, has thus considerable potential to improve the organoleptic acceptability of soy-based dairy substitutes and thereby improve the availability of clean fresh water in areas of the world where economically disadvantaged communities have limited access to the resource. Commercialization of ZOTO by Circa will be under the tradename Laiscent<sup>TM</sup>.

# • Dihydrolevoglucosenone as a new dipolar aprotic solvent

Dihydrolevoglucosenone can serve as a non-toxic replacement for N-methylpyrrolidone (NMP) and dimethylformamide (DMF), and can be made in a solvent-free fashion. This has created a high volume sales opportunity currently being exploited by the Circa company: their new FC5 pilot plant

<sup>&</sup>lt;sup>4</sup> Blattner, R., Furneaux, R. H., Mason, J. M. and Tyler, P. C., *Pesticide Science*, **31**, 419 – 435, (1991)

<sup>&</sup>lt;sup>5</sup> Flourat, A. L.; Peru, A. A. M.; Teixeira, A. R. S.; Brunissen, F.; Allais, F., Chemo-enzymatic synthesis of key intermediates (S)gamma-hydroxymethyl-alpha,beta- butenolide and (S)-gamma-hydroxymethyl-gamma-butyrolactone via lipase-mediated Baeyer-Villiger oxidation of levoglucosenone. *Green Chemistry* **2015**, *17* (1), 404-412.

<sup>&</sup>lt;sup>6</sup> Allais, f. r. d. r., reims, reims, f-51100, fr), flourat, amandine (20 rue alexandre henrot, reims, reims, f-51100, fr), peru, aurélien (37 e rue prieur de la marne, reims, f-51100, fr), teixeira, andreia (64 rue emile zola, reims, reims, f-51100, fr), brunissen, fanny (137 boulevard pommery, reims, reims, f-51100, fr), spinnler, henry eric (32 bis avenue de la division leclerc, sèvres, f-92310, fr), method for transforming levoglucosenone into 4-hydroxymethyl butyrolactone or 4-hydroxymethyl butenolide. wo/2015/165957, 2015.

will convert a large amount of the produced LGE to dihydrolevoglucosenone (commercialized as CyreneTM). The substitution of NMP & DMF with benign non-toxic Cyrene is expected to satisfy the growing demand for low toxicity solvents. Cyrene<sup>™</sup> has passed all the toxicity test requirements under Annexe VII of the REACh Regulations permitting its import into the European Union.

# • The conversion of LGE '1,6-hexandiol' and '1,2,6-hexantriol' and beyond

We have put significant emphasis on converting LGE to 1,6-hexandiol and 1,2,6-hexantriol in Figure 2. The following list of DuPont patents illustrates the strong, and on-going, interest of DuPont as an example, in the use of these bio-momomers [2013-2015]:

Allgeier, A. M. O. P., CA, US), Desilva, Namal (Wilmington, DE, US), Korovessi, Ekaterini (Wilmington, DE, US), Menning, Carl (Newark, DE, US), Ritter, Joachim C. (Wilmington, DE, US), Sengupta, Sourav Kumar (Wilmington, DE, US) PROCESS FOR PREPARING 1, 6-HEXANEDIOL. 20130172629, **2013** 

Allgeier, A. M. W., DE, US), Corbin, David Richard (West Chester, PA, US), De Silva, Wathudura Indika Namal (Wilmington, DE, US), Korovessi, Ekaterini (Wilmington, DE, US), Menning, Carl Andrew (Newark, DE, US), Ritter, Joachim C. (Wilmington, DE, US), Sengupta, Sourav Kumar (Wilmington, DE, US) Process for preparing 1, 6-hexanediol. 8889922, **2014** 

Allgeier, A. M. W., DE, US), De Silva, Wathudura Indika Namal (Wilmington, DE, US), Korovessi, Ekaterini (Wilmington, DE, US), Menning, Carl Andrew (Newark, DE, US), Ritter, Joachim C. (Wilmington, DE, US), Sengupta, Sourav Kumar (Wilmington, DE, US), Stauffer, Christina S. (Wilmington, DE, US) Process for preparing 1, 6-hexanediol. 8962894, **2015** 

Allgeier, A. M. W., DE, US), Corbin, David Richard (West Chester, PA, US), De Silva, Wathudura Indika Namal (Rahway, NJ, US), Korovessi, Ekaterini (Wilmington, DE, US), Menning, Carl Andrew (Newark, DE, US), Ritter, Joachim C. (Wilmington, DE, US), Sengupta, Sourav Kumar (Wilmington, DE, US) Process for preparing 1,6-hexanediol. 8889912, **2014** 

We would also like to outline that DuPont's interest in (bio-derived) diols relates also to their strong activities in the field of synthetic textile fibres. It's exactly because of their success with the polyester fibre Sorona®, which is based on 1,3-propane diol, produced by fermentation of sucrose, that DuPont is currently showing considerable interest in the production of (bio-derived) 1,6-hexane diol and other (bio-derived) C6 and C5 alcohols. And for that purpose the catalytic high-pressure hydrogenation and hydrodeoxygenation of LGE is a very interesting route.

# • The conversion of LGE to HMF

HMF is widely considered as a future platform molecule. Recent developments in its utilization include the work on chloromethylfurfural (CMF) (led by Prof. Mark Mascal ) aimed at circumventing problems due to HMF's high reactivity by capturing HMF through chlorination. The alternative to this, and a chlorine-free method, would be via LGE as it is the more stable isomer of HMF – and as tonnes production of LGE is underway this could become a very real and appealing option in the near future.

# Reference experiment using softwood pulp and softwood sawdust

Relevant experiments are described in our associated patent.<sup>7</sup> For the benefit of this manuscript, we have performed reference experiments on both sulphuric acid (0.5 wt%) impregnated thermomechanical softwood pulp and softwood sawdust (by soaking it in a 0.002 M aqueous solution). These acid-impregnated materials were then subjected to microwave irradiation, in air under ambient pressure, following the same protocol as outlined for the original process in the manuscript/supplementary material. In this specific case removal of the extraction solvent (acetone) afforded 1 - 2% of a brown tarry liquid which was analysed by gas chromatography. No LGE was detected meaning that the yields of LGE obtained from lignocellulose, which does not have the unusual lignin morphology described in the manuscript, is <0.001 wt% based on the weight of pulp or sawdust treated. This negligible yield was obtained despite the much higher proportions of cellulose (typically 37 – 48 wt%) typically found in unprocessed softwoods than those reported for the CSHL in the manuscript.<sup>8</sup>

<sup>&</sup>lt;sup>7</sup> Method for producing levoglucosenone, inventors: Mario De bruyn, Vitaliy Budarin and James H. Clark PCT/GB2016/051095

<sup>&</sup>lt;sup>8</sup> Petersen, R.C., Chapter 2: 'The Chemical Composition of Wood', in Rowell, R.M. (ed.) 'The Chemistry of Solid Wood – Advances in Chemistry Series No. 207', Washington, DC: ACS (1984)

# ICP analysis on CSHL

# • Mg. Al, Ca, Fe, Mn and Zn can act as Lewis acid centers

Element	Method 1		Method 2		Method 3	
	No carrier ga	lS	Use of helium		Use of high energy	
			carrier gas		helium carri	er gas
Na	23 Na [	No Gas ]	23 Na [He]		23 Na [HEHe]	
	Conc.[ppb]	Conc. RSD	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD
	1497.56	1.4	1330.92	3.8	1466.58	1.3
µg Na / g dry CSHL	664.11		590.21		650.37	
Mg	24 Mg [	No Gas ]	24 Mg	; [He]	24 Mg	[HEHe]
C	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	187.29	0.7	168.15	8	181.38	1.4
μg Mg / g dry CSHL	83.06		74.57		80.43	
Al	27 Al [	No Gas ]	27 Al	[ He ]	27 Al	HEHe ]
	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD
	84.75	0.9	82.48	4.5	79.85	4.6
µg Al / g dry	37.58		36.58		35.41	
CSHL						
V	30 K [	No Gas 1	30 K	[H <sub>0</sub> ]	30 K I	HEHe 1
K	Conc. [ppb		Conc. [ppb		Conc. [ppb	
	]	Conc. RSD	]	Conc. RSD	]	Conc. RSD
	728.9	1.4	648.17	2.5	702.16	2
μg K / g dry	323.24		287.44		311.38	
CSHL						
Ca	44 Ca [	No Gas 1	44 Ca	[He]	44 Ca	HEHe 1
Ca	Conc. [ppb		Conc. [ppb		Conc. [ppb	
	]	Conc. RSD	]	Conc. RSD	]	Conc. RSD
	1998.94	2.2	1981.29	5.5	1858.58	1.3
μg Ca / g dry	886.45		878.62		824.2	
CSHL						
Cr	52 Cr [	No Gas 1	52 Cr	[He]	52 Cr	HEHe 1
	Conc. [ppb	Conc DOD	Conc. [ppb	Cono DOD	Conc. [ppb	Cone DCD
	]	Conc. KSD	]		]	
	26.31	2.3	24	3.7	25.14	1.1
μg Cr / g dry CSHL	11.67		10.64		11.15	

Mn	55 Mn [	No Gas ]	55 Mn	[ He ]	55 Mn	[HEHe]
	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	164.78	2.5	162.56	2.7	153.69	0.4
µg Mn / g dry CSHL	73.07		72.09		68.16	
Fo	56 Fe [	No Gas 1	56 Fe	[He]	56 Fe I	HFHe 1
re	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	160.55	3.5	153.92	2	158.02	0.7
µg Fe / g dry CSHL	71.2		68.26		70.08	
Ni	60 Ni [	No Gas ]	60 Ni	[ He ]	60 Ni	HEHe ]
	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD
	18.59	2.2	18.23	4.3	18.27	1.8
μg Ni / g dry CSHL	8.24		8.08		8.1	
Cu	63 Cu [	No Gas ]	63 Cu	[ He ]	63 Cu	[HEHe]
	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD	Conc. [ppb ]	Conc. RSD
	8.95	0.9	8.53	3.5	8.85	2.8
µg Cu / g dry	3.97		3.78		3.92	
Zn	66 Zn [	No Gas ]	66 Zn	[ He ]	66 Zn	[HEHe]
	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	29.46	2.8	28.77	1.8	29.24	1.3
μg Zn / g dry CSHL	13.06		12.76		12.97	
Мо	95 Mo [	No Gas ]	95 Mo	[ He ]	95 Mo	[HEHe]
	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	12.15	0.7	7.79	5.1	7.42	7.8
μg Mo / g dry	5.39		3.45		3.29	
Cont						
Ba	137 Ba	[ No Gas ]	137 Ba	a [He]	137 Ba	[HEHe]
	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD	Conc. [ppb	Conc. RSD
	125.48	2.1	114.78	1.2	113.46	0.5
			<b>70</b> 0		50.01	

# Potential reasons for the non-observation of levoglucosenone from acid treated softwood/sawdust

#### Many explanations are possible:

- 1) In native biomass such as Spruce softwood the cellulosic, hemicellulose and lignin components are highly intertwined. Importantly the literature states that the presence of lignin stabilizes cellulose against dehydration and thermal oxidation at starting temperatures of pyrolysis (120–280 °C).<sup>1</sup> This phenomenon has been explained by lignin's tendency to scavenge free radicals. It has also been demonstrated that this protective action of lignin enables a high yield of levoglucosan at 300-400 °C. The element of 'lignin-protected-anhydrosugars' was also extented towards their observation of levoglucosenone formation. This does fit the nonobservance of levoglucosenone formation during the performed pyrolysis of Spruce softwood sawdust at 180 °C. Furthermore it also reinforces our hypothesis that lignin is playing a beneficial and stabilizing action: CSHL is the product of a biorefinery process in which softwood has been treated with dilute sulphuric acid at 200 °C. It is known that in this process the molecular weight of the lignin is decreased, and together with its hydrophobicity and the surface tension effects of water, makes that it then forms small spherical lignin droplets on the cellulose fibre surface.<sup>2</sup> Thus the remaining lignin after the biorefinery process is no longer protective of the cellulose fibre and may well have engaged now in stabilizing levoglucosenone. The presence of lignin also restricts the swelling of cellulose which contrasts markedly with the fact that cellulose-swelling, by acids/sulfolane, is needed to form levoglucosenone.<sup>1</sup>
- 2) Related to point 1 we also would like to highlight that the CSHL was obtained from the treatment of Spruce softwood with dilute sulphuric acid at 200 °C, and when analysing the acetone extracts of CSHL we have not detected any levoglucosenone (see figure 5S). This is strongly indicative that levoglucosenone formation from Spruce softwood using H<sub>2</sub>SO<sub>4</sub>, and in the absence of any stabilizing agent such as sulfolane or THF, is not evident. Also, the Circa company has never observed the formation of levoglucosenone in significant yields from biomass when not employing sulfolane in their processes.
- 3) The role of sulfolane in the formation of levoglucosenone from cellulose has only been reported a few times. Kawamoto et al. suggested that it prevents the anhydrosugars (in their manuscript mainly levoglucosan) from polymerizing keeping them in a liquid state.<sup>3</sup> In our process no sulfolane, THF or ionic liquid is present and consequently we attribute the LGE stability in our system to the low reaction temperature of 180 °C. Additionally, the literature states that the absence of hemicelluloses is a beneficial factor in the formation of anhydrosugars.<sup>1</sup> This aligns very well with the fact that the CSHL has very little residual hemicellulose, as almost all of it is removed during the biorefinery step (this is very well documented in the manuscript).
- 4) In the biorefinery process, treatment of the inert crystalline cellulose with dilute sulphuric acid at 200 °C increases the amount of amorphous cellulose and glucose mono/oligosaccharides. Thus

the saccharides become available for further processing either by enzymes or for the inaccessible saccharides (see manuscript) for the production of levoglucosenone.

We would also like to point out that the paper by the Huber group [*Ref 15 in the manuscript: F. Cao, T. Schwartz, D. McClelland, S. Krishna, J. Dumesic and G. Huber, Energy & Environmental Science, 2015*] on levoglucosenone formation from cellulose in the presence of  $H_2SO_4$ /THF also states that levoglucosenone can only be formed when using low cellulose loadings and very low water contents. Softwood sawdust has a high cellulose content and, apart from its intrinsic water content, we also needed to add significant amounts of water in the acid treatment.

# References to this section

1. J. Zandersons, A. Zhurinsh, G. Dobele, V. Jurkjane, J. Rizhikovs, B. Spince and A. Pazhe, *Journal of Analytical and Applied Pyrolysis*, 2013, **103**, 222-226.

2. L. Kumar, V. Arantes, R. Chandra and J. Saddler, *Bioresource Technology*, 2012, 103, 201-208.

3. H. Kawamoto, W. Hatanaka and S. Saka, *Journal of Analytical and Applied Pyrolysis*, 2003, **70**, 303-313.

# Brief discussion of the mechanistic formation of levoglucosenone

The publication by Kawamoto on "catalytic pyrolysis of cellulose in sulfolane with some acidic catalysts" summarizes the three potential routes to levoglucosenone adequately<sup>6</sup> and we quote:

"Although ratio between levoglucosenone, furfural, and 5-HMF is very similar, the levoglucosenone/levoglucosan ratio is quite different between cellulose and levoglucosan pyrolysis. For example, the molar ratios after 2min of pyrolysis are 4.8 and 1.6 for cellulose and levoglucosan pyrolysis, respectively. If levoglucosenone is formed only from levoglucosan, the ratio observed in cellulose pyrolysis should be equal to or even smaller than that in levoglucosan pyrolysis. The experimental facts suggest that another pathway also exists in levoglucosenone formation along with the pathway via levoglucosan. Details of this pathway and the relative importance between these pathways are unknown at present, but dehydration prior to levoglucosan formation is also suggested in the pyrolysis of cellulose impregnated with acid catalyst.8–10,13 Shafizadeh et al.9 reported 1,4:3,6-dianhydroa-d-glucopyranose as an intermediate for levoglucosenone compared with the retention of the glucose moiety in the pyrolysis residue, and they concluded that dehydration proceeds in the solid state prior to depolymerization."

With respect to the recent literature, levoglucosenone formation from levoglucosan has also been reported by the Huber group<sup>7, 8</sup> Concerning the non-levoglucosan route to levoglucosenone, the recent publications by Sarotti<sup>9</sup> and two consecutive publications by Shanks/Broadbelt et al.<sup>10, 11</sup> are very illustrative. More specifically schemes 1 & 2 in the Sarotti paper, and their discussion, are very revealing. For the convenience of the referee we include here the main two relevant passages in the Sarotti paper:

"The generation of levoglucosenone, formally a double dehydration of levoglucosan, represents an example of a transformation whose mechanism has not been fully elucidated yet. For instance, the complete absence of the transposed enone isolevoglucosenone (3) in the pyrolysates represents an experimental observation important to unravel. The first attempt to rationalize levoglucosenone formation was made by Broido and co-workers, and is depicted in Scheme 1. 8 The key transformation, that defines the regiochemistry of the reaction products, involves a 1,2-hydride shift of the cation resulting from the dehydration of the OH group at C-3 of 1. The pseudosymmetry of the molecule allows two plausible shifts, namely A and B. In path A, the H-2 shifts to install the carbonyl group at C-2, leading to the formation of 2, whereas in path B the hydride shift now occurs with the H-4 atom resulting in the ultimate generation of 3. To explain the perfect selectivity in the dehydration process, the authors suggested that cation A should be more stabilized than cation B because of the proximity with the 1,6-anhydro oxygen atom.8 However, according to calculations carried out in the present work at the high accuracy CBS-QB3 method, the regioselectivity of this dehydration step should be low. Very small energy differences between cations A and B (DDG = 0.25 kcal/mol) and between the two 1,2-hydride shift transition structures connecting them with their precursor (DDG = 0.21 kcal/mol) were computed.9 These results are in perfect agreement with a recent study of Assary and Curtiss, in which they provided further computational evidence of the dehydration process from 1 to 2 and 3, in which the B3LYP/6-31G(2df,p) energy profiles computed for both pathways are similar in energy.10 A different approach was done by Shafizadeh et al. suggesting 1,4:3,6-dianhydro-a-D-

glucopyranose (4), obtained from 1, as a possible pyrolytic precursor of 2 (Scheme 2).11 Interestingly, this proposal successfully explains the absence of 3 in the pyrolysates. On the other hand, Furneaux et al. proved that 2 can undergo pyrolytic deformylation (via a [5+2] dipolar cycloreversion) to give formaldehyde (5) and 3-oxidopyrylium (6), a highly reactive species that can further dimerize or react with another molecule of 2 to afford adducts 7 and 8 in a 4:3 ratio.12 The detection of these compounds in the pyrolysates evidenced not only the proposed degradation path, but also provided an explanation of the lower yield in which 2 is typically obtained with respect to 1. Later, the same group found a similar chemical behavior for 3: after heating, it suffers the loss of formaldehyde to afford 6, that is further trapped by unreacted enone to yield the 1,3-dipolar adducts 9 and 10 in a 3:1 ratio (Scheme 3).13"

These results provide enough computational evidence to refute one of the original hypotheses formulated earlier. It would be difficult to explain the absence of **3** and its adducts with 3-oxidopyrylium (**9** and **10**) in the pyrolysis crudes without resorting to the idea that isolevoglucosenone does not form at all during the pyrolytic degradation of cellulosic materials. This, along with other recent reports, suggest that levoglucosenone should not be formed directly from levoglucosan, but rather from another intermediate, such as 1,4:3,6-dianhydro- $\alpha$ -d-glucopyranose.<sup>11</sup>

As to the two papers by the groups of Brent Shanks and Linda Broadbelt we like to refer the referee to Scheme 4 in their first paper<sup>11</sup> which does not show the involvement of levoglucosan in the formation of levoglucosenone.

## References to this section

- 6. H. Kawamoto, S. Saito, W. Hatanaka and S. Saka, *Journal of Wood Science*, 2007, **53**, 127-133.
- 7. F. Cao, T. J. Schwartz, D. J. McClelland, S. H. Krishna, J. A. Dumesic and G. W. Huber, *Energy & Environmental Science*, 2015, **8**, 1808-1815.
- 8. Y.-C. Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland and G. W. Huber, *Journal of Physical Chemistry C*, 2009, **113**, 20097-20107.
- 9. A. M. Sarotti, *Carbohydrate Research*, 2014, **390**, 76-80.
- 10. X. Zhou, M. W. Nolte, B. H. Shanks and L. J. Broadbelt, *Industrial & Engineering Chemistry Research*, 2014, **53**, 13290-13301.
- 11. X. Zhou, M. W. Nolte, H. B. Mayes, B. H. Shanks and L. J. Broadbelt, *Industrial & Engineering Chemistry Research*, 2014, **53**, 13274-13289.

# Saccharide analysis

# **Solubles**

- Weight 50 mg x 3 of biomass
- Also record weight of the 2ml tubes that they are weighed into.
- Wash with 1.5ml ethanol and vortex
- Spin down for 20 min
- Remove supernatant, and air dry
- Add 1ml 90% aqueous DMSO and leave rocking overnight.
- Spin down for 20 min
- Wash 4 times with ethanol (remove supernatant; add 1ml ethanol; vortex; spin for 10mins; repeat)
- Dry in speed vac (for 90 mins 60oC)
- Weight samples after extractions
- Determine the % of solubles

# Analysis of matrix polysaccharides

# Materials

- Dry samples
- Screw cap tubes
- 2M Trifluororoacetic acid = 11.4 g in 50 ml (or 3ml 99.5% TFA and 17ml  $dH_2O$ )
- Compressed Argon
- Monosaccharide standards

- Standard sugar mixture of nine monosaccharides (arabinose, fucose, galactose, galacturonic acid, glucose, glucuronic acid, mannose, rhamnose, and xylose) each at 100  $\mu$ M.. Each monosaccharide is in a 10mM stock solution (100X). Standard preparation described in

R:\rsrch\sjmm\lab\Rachael\Protocols\Monosaccharide stds. The preparation of the standards is done by pipetting 250, 500, and 700  $\mu$ l in screw cap tubes and drying them up. Proceed to hydrolysis in the same way as with the samples.

# Method

# Day 1

- Weigh 5 mg of sample in screw cap tubes

- Dry all the samples and standards (250, 500, 700)

# Day 2

- In the fume hood, hydrolyse by adding 0.5 ml 2 M TFA. Flush the vials with dry Argon, place the cap, and mix well. Wipe argon nozzle with ethanol tissue between samples to prevent contamination.

- Heat the vials @ 100  $^{\circ}$ C for 4 h and mix several times during hydrolysis.

- Cool the vials at room temperature and evaporate completely in centrifugal evaporator with fume extraction overnight.

TFA is Harmful by inhalation. Causes severe burns. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Avoid inhalation of vapour or mist. No liquid disposal: should be evaporated UNDER FUME HOOD.

# Day 3

- Add 500  $\mu L$  of Propan 2-ol, mix , and evaporate.
- Repeat
- Resuspend the samples in 200µl of ELGA water. Mix well. Mix again.
- Take the supernatant into a new tube.

- Filter 100  $\mu$ l with 0.45  $\mu$ m PTFE filters. Use 1 ml syringes to filter and put the samples into HPLC vials.

Use the rest of the samples to quantify reducing sugars by DNS or MBTH.

# **Crystalline Cellulose Content**

Sample preparation:

- 1. Weigh out 5mg plant material into a 2ml screw capped tube.
- 2. Add 500ul 2M TFA

TFA is Harmful by inhalation. Causes severe burns. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Avoid inhalation of vapour or mist. No liquid disposal: should be evaporated UNDER FUME HOOD.

- 3. Flush with Argon.
- 4. Incubate for 4hrs at 100°C, shaking the samples every hour.
- 5. Evaporate TFA in the centrifugal evaporator.
- 6. Wash with 500ul  $dH_2O$  twice without disturbing the pellet.
- 7. Dry pellet in the centrifugal evaporator.

Use pellet from Matrix polysaccharide protocol if this work has been done.

Updegraff method:

- 1. Add 1 ml of Updegraff reagent (Acetic acid: nitric acid: water, 8:1:2 v/v) to the TFA pellet.
- 2. Cap tube tightly, vortex, and heat in a heating block at 100°C for 30 min. As a result of this treatment only crystalline cellulose remains insoluble in the pellet.
- 3. Cool samples in the block on ice to room-temperature or cooler.
- 4. Centrifuge samples at 10,000 rpm for 15 min.
- 5. Discard supernatant ensuring that the pellet is not disturbed and no material from the pellet is removed.
- 6. Add 1.5 ml of water, shake, centrifuge, and discard supernatant as done above.
- 7. Repeat washing procedure 3 additional times using 1.5 ml of acetone.
- 8. Air dry pellet very gently with air, or let dry on bench overnight.
- The pellet (crystalline cellulose) is now completely hydrolyzed into glucose by what is called a Saeman hydrolysis. For this purpose add 90 μl 72% Sulfuric acid (made up by weight) to the tube.
- 10. Incubate at room temperature for 4 hours on platform rocker (dissolves H-bonds).
- 11. Add 1890 µl water and vortex (dilutes down to 3.2% sulphuric acid). Heat for 4h at 120°C.
- 12. Centrifuge samples at 10,000 rpm for 5 min. There might be some brown insoluble material, lignin, remaining in the tube.

Glucose quantification:

- 1. The glucose content of the supernatant is assayed using the colorimetric Anthrone assay.
- 2. For the standard curve use a 1mg/ml glucose stock (stored at 0°C). The Anthrone reagent is freshly prepared.
- 3. Pipette the following amounts of solutions into 2ml tubes:

	Sample (ul)	dH <sub>2</sub> O (ul)	Anthrone Reagent (ul)
Blank	0	400	800
Std 0.5	2	398	800
Std 1	4	396	800

Std 2	8	392	800
Std 4	16	384	800
Std 6	24	376	800
Std 8	32	368	800
Std 10	40	360	800
Sample	40	360	800

- 4. Incubate tubes at 80°C for 30 min in heating block. Glucose containing samples turn from yellow into blue-green.
- 5. Let the samples cool to room temperature and shake thoroughly.
- 6. Pipette 200ul of samples and standards into an optical plate.
- 7. Read the absorption of the plate at 620nm.
- 8. Glucose (and hence crystalline cellulose content) is calculated based on the absorbance compared to the standard curve established on the same plate.

# Solutions:

1. Updegraff Reagent

Acetic Acid: Nitric Acid: Water (8:1:2 v/v)

# For 55ml:

- 40ml Acetic Acid
- 7.69ml 65% Nitric Acid
- 7.31ml dH<sub>2</sub>O
- 2. Anthrone Reagent

2 mg anthrone/ ml concentrated sulphuric acid Make fresh each time



https://www3.epa.gov/climatechange/ghgemissions/sources/transportation.html

# Climate Change Sources of Greenhouse Gas Emissions



#### **ON THIS PAGE**

**Emissions and Trends** 

#### Reducing Emissions from Transportation

The Transportation sector includes the movement of people and goods by cars, trucks, trains, ships, airplanes, and other vehicles. The majority of greenhouse gas emissions from transportation are  $CO_2$  emissions resulting from the combustion of petroleum-based products, like gasoline, in internal combustion engines. The largest sources of transportation-related greenhouse gas emissions include passenger cars and light-duty trucks, including sport utility vehicles, pickup trucks, and minivans. These sources account for over half of the emissions from the sector. The remainder of greenhouse gas emissions comes from other modes of transportation, including freight trucks, commercial aircraft, ships, boats, and trains as well as pipelines and lubricants.

Relatively small amounts of methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) are emitted during fuel combustion. In addition, a small amount of hydrofluorocarbon (HFC) emissions are included in the Transportation sector. These emissions result from the use of mobile air conditioners and refrigerated transport.

## **Emissions and Trends**

In 2014, greenhouse gas emissions from transportation accounted for about 26% of total U.S. greenhouse gas emissions, making it the second largest contributor of U.S. greenhouse gas emissions after the <u>Electricity sector</u>. Greenhouse gas emissions from transportation have increased by about 17% since 1990. This historical increase is largely due to increased demand for travel and the limited gains in fuel efficiency across the U.S. vehicle fleet. The number of vehicle miles traveled by passenger cars and light-duty trucks increased 37% from 1990 to 2014. The increase in travel miles is attributed to several factors, including population growth, economic growth, urban sprawl, and low fuel prices during the beginning of this period. Between 1990 and 2004, average fuel economy among new vehicles sold annually declined, as sales of light-

Total U.S. Greenhouse Gas Emissions by Economic Sector in 2014



<u>Tons of CO<sub>2</sub> equivalent</u>

\* Land Use, Land-Use Change, and Forestry in the United States is a net sink and offsets

#### Greenhouse Gas Emissions: Transportation Sector Emissions | Climate Change | US EPA

duty trucks increased. However, new vehicle fuel economy began to improve in 2005, largely due to a lower light-duty truck market share and higher fuel economy standards.

Learn more about <u>Greenhouse Gas Emissions from Transportation</u>. To learn about projected greenhouse gas emissions to 2020, visit the <u>U.S. Climate Action Report 2014 (PDF)</u> (310 pp., 23.1 MB).

approximately 11% of these greenhouse gas emissions.

All emission estimates from the *Inventory of U.S.* Greenhouse Gas Emissions and Sinks: 1990-2014

#### **Related Links**

- <u>Transportation and Climate</u>
- EPA and U.S. DOE Fuel Economy
- <u>SmartWay</u>

•

- <u>On The Road</u>
- Smart Growth
- <u>Renewable Fuel Standard</u>
- <u>U.S. Inventory's section on Fossil</u>
   <u>Fuel Combustion</u>



Note: Emissions involved in the consumption of electricity for transportation activities are included above, but not shown separately (as was done for other sectors). These indirect emissions are negligible, accounting for less than 1%

of the total emissions shown in the graph. Note: All emission estimates from the *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2014*.

# **Reducing Emissions from Transportation**

There are a variety of opportunities to reduce greenhouse gas emissions associated with transportation. The table shown below categorizes these opportunities and provides examples. For a more comprehensive list, see <u>Chapter 5 of the Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel</u> on Climate Change. **EXIT Disclaimer** 

EPA's vehicle greenhouse gas rules will save consumers \$1.7 trillion at the pump by 2025, and eliminate six billion metric tons of GHG pollution.

#### Туре How Emissions are Reduced Examples Fuel Switching Using fuels that emit less CO<sub>2</sub> than fuels currently being used. Alternative sources Using public buses that are fueled by can include biofuels; hydrogen; electricity from renewable sources, such as wind and compressed natural gas rather than gasoline solar; or fossil fuels that are less CO<sub>2</sub>-intensive than the fuels that they replace. or diesel. Learn more about Alternative and Renewable Fuels. Using electric or hybrid automobiles, provided that the energy is generated from lower-carbon or non-fossil fuels. Using renewable fuels such as low-carbon biofuels. Improving Fuel Efficiency Using advanced technologies, design, and materials to develop more fuel-efficient Developing advanced vehicle technologies with Advanced Design, vehicles. such as hybrid vehicles and electric vehicles, Materials, and that can store energy from braking and use it Technologies Learn about EPA's vehicle greenhouse gas rules. for power later. Reducing the weight of materials used to build vehicles. Reducing the aerodynamic resistance of vehicles through better shape design. Improving Operating Adopting practices that minimize fuel use. Reducing the average taxi time for aircraft. Practices Improving driving practices and vehicle maintenance. • Driving sensibly (avoiding rapid acceleration Learn about how the freight transportation industry can reduce emissions through and braking, observing the speed limit). EPA's SmartWay Program. Reducing engine-idling. • Improved voyage planning for ships, such as through improved weather routing, to increase fuel efficiency.

## Examples of Reduction Opportunities in the Transportation Sector

Reducing Travel Demand	Employing urban planning to reduce the number of miles that people drive each day. Learn about EPA's <u>Smart Growth Program</u> .	<ul> <li>Building public transportation, sidewalks, and bike paths to increase lower-emission transportation choices.</li> </ul>
	Reducing the need for driving through travel efficiency measures such as commuter, biking, and pedestrian programs. See a list of links to state, local, regional travel-efficiency programs.	<ul> <li>Zoning for mixed use areas, so that residences, schools, stores, and businesses are close together, reducing the need for driving.</li> </ul>

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#### **Crude Oil Prices - 70 Year Historical Chart**

Description: Interactive chart of historical monthly West Texas Intermediate (WTI or NYMEX) crude oil prices per barrel back to 1946. The price of oil shown is adjusted for inflation using the headline CPI and is shown by default on a logarithmic scale. The current month is updated on an hourly basis with today's latest value. The current price of WTI crude oil as of 09:33 AM EDT on April 18, 2016 is \$38.69 per barrel.

#### Chart Tips: 1) All charts are fully interactive.

2) Use the links above the chart to zoom to common date ranges.

3) Left click and drag your mouse to drill down to a custom date range.

4) Use the scrollbar at the top of the chart to move back and forth between time periods while zoomed.

✓ Log Scale ✓ Inflation-Adjusted ✓ Show Recessions

Click and drag in the plot area or select dates: 5 Years | 10 Years | 20 Years | 30 Years | 50 Years | All Years



#### **Related Charts**

WTI Crude Oil - 10 Year Daily (http://www.macrotrends.net/2516/wti-crude-oil-prices-10-year-daily-chart)

Interactive chart showing the daily closing price for West Texas Intermediate (NYMEX) Crude Oil over the last 10 years. The prices shown are in U.S. dollars.

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# OUTLOOK '16: The year the world drowned in oil

#### 21 December 2015 14:00 Source: ICIS News

#### By Kawai Wong

LONDON (ICIS)--The international <u>crude oil (/energy/crude-oil/)</u> market is rarely stable and 2016 will not disappoint. Iranian crude oil returns to the international markets adding to the global oversupply while brimming US crude stockpiles is seriously testing storage limits. South Korea's freight rebate policy reform could potentially skew international oil pricing benchmarks while China's expected launch of a crude oil derivatives contract will challenge Brent and WTI benchmark status.

In the first quarter of next year, Iranian crude oil is expected to return to international oil markets after the International Atomic Energy Agency (IAEA) verifies that Iran has complied with the Joint Comprehensive Plan of Action (JCPOA) to curb Iran's nuclear capability, signed 14 July.

Iran's crude oil exports currently stand at 1.10m bbl/day and production at 3.12m bbl/day, OPEC data shows. Iran believes it can raise production quickly by 500,000 bbl/day and incrementally add another 500,000 bbl/day by the end of the year. But before this flood of oil, there will be a tsunami wave that will hit the market first.

Since Europe raised sanctions against Iran in 2012 causing EU imports of Iranian oil to come to a complete halt, much of the excess crude oil produced since sanctions has been stored while production was drawn down.

The International Energy Agency estimates that Iran has 40m barrels of crude oil stored on vessels and these are set to sail as soon as the IAEA gives the green light.



### The monthly global ICIS Petrochemical Index (IPEX)

#### (/contact/request-free-

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IPEX provides a capacity-weighted measure of the average change in petrochemical prices over time.

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#### Pressure on the benchmark

The first quarter could also see some potential downward pressure on the UK North Sea Forties Blend and the Dated BFOE benchmark and variants. This unintentional pressure is caused by the South Korean Energy Ministry, which has reformed its crude oil import freight rebate policy for importing non-Middle Eastern crude.

The freight rebate, designed to widen South Korea's sources of crude and shift away from the volatile Middle East, gave importers a rebate on the freight difference. However from early 2016 the programme will exclude spot deals favouring the security of term deals only.

South Korea has developed a taste for Forties. According to GAC shipbrokers, South Korea imports around 2.00-6.00m barrels/month, equating to three to 10 cargoes/month since 2012 when exports to South Korea began.

If South Korean demand disappears, this could not only pressure the value of Forties but potentially pressure the benchmark because the daily value of Forties is almost the de facto physical grade used in the daily benchmark calculation for around 70% of all physical crude oils.

The benchmark calculation picks the cheapest of the Brent, Forties, Oseberg and Ekofisk as part of the benchmark calculation and it is usually Forties because of its relative poorer quality. Additionally, the quality of Forties itself is also deteriorating with a rising amount of sulphuric Buzzard crude in the blend, according to BP data.

Forties is a blend of crude oils from different oilfields and the largest contributor is Nexen-operated Buzzard oil field, which has made Forties increasingly sulphuric since 2007 when it was added to the blend. Nexen is a subsidiary of China National Offshore Oil Corporation.



### ICIS Dated BFOE

#### China goes international

Later in the year, China's national currency, the renminbi, will become more international as it enters the International Monetary Fund's (IMF) Special Drawing Rights (SDR) basket of currencies, which includes the US dollar, the euro, the British Pound and the Japanese Yen.

The SDR is an international reserve asset defined and maintained by the IMF. Members can buy and sell SDRs in return for freely usable currencies of IMF members and can be used to provide liquidity to governments and major institutions in exceptional circumstances such as the 2009 financial crisis.

The addition of the Renminbi into the SDR basket in September may roughly coincide with the launch of the long delayed crude oil derivatives contract planned by the Shanghai International Energy Exchange (INE), which sources say are close to finalising the product.

The Shanghai Crude oil futures contract will be renminbi-denominated and fully open to the International market. Its initial years is likely to see the contract dominated by Chinese domestic refiners for hedging purposes.

Overtime it is expected that the contract will eventually win a significant portion of the trillion dollar crude oil futures market away from the incumbents ICE Brent and NYMEX WTI simply because China is now the largest importer of crude oil, <u>petroleum (/energy/petroleum/)</u> products and other liquids since September 2013, according to data from the Energy Information Administration (EIA).

#### Supply volatility

The 2016 story is inevitably going to be oversupply, but the effect on pricing is selective due to differing crude oil qualities. Iran's crude oil is mostly sour, much like Russia's with similar export destinations, where one is the Mediterranean/southern Europe.

Sanctions against Iran benefitted Russia's Urals and narrowed the price spread against the better quality light-sweet grades such as Algeria's Saharan Blend and on occasion even surpassed its value. The spread will widen next year and sour crude exports to southern Europe will be a buyers' market, while lighter grades in the region will at least sustain some strength due to its higher quality.

But there is an unpredictable source of volatile light-sweet crude that could return from war torn Libya where production was last heard quoted by the Libyan National Oil Corporation (NOC) at 375,000 bbl/day, well below its pre-civil war levels at 1.60m bbl/day. The rival government's latest agreement will see both sides form a unity government and have elections within two years, but the fighting goes on and now also with the Islamic State.

The global oil market may also see a stable source of crude oil from the US which cannot export domestically produced oil and only tiny volumes of non-US oil under the Energy Policy and Conservation Act 1975. The reasons for reversing the export ban are mounting, literally, as the US is seriously running out of storage space and hitting record high stockpiles in April.

Although the story is oversupply, there is fear that the worsening conflict in Yemen could spill over to Bab Al Mandeb, the strait where around 4.00m bbl/day of oil flows, potentially cutting this supply to the market, which will more than wipe out Iran's renewed contribution.

#### Decommissioning brought forward

The flood of crude oil from OPEC producers has forced US shale oil producers to cut back production. According to data from the EIA, US shale oil production fell each month since February as production remains uneconomical.

Although some US shale oil producers can return to production once oil prices are more favourable, for some mature regions such as the North Sea, the low oil price is already pushing producers to bring forward decommissioning plans, according to the UK lobbyist group, Oil and <u>Gas (/energy/gas/)</u> UK (OGUK).

Bringing forward decommissioning plans in the North Sea will forever shut out a supply of crude oil because the oil cannot be produced even if prices recover since the infrastructure for production would have been removed already and at immense cost.

Decommissioning the UK North Sea over the next 10 years will cost around £17bn to scrap 79 platforms and plugging 1,200 oil wells, according to OGUK.

The US Gulf of Mexico, which provides around 25% of total US conventional crude oil production, is also facing a similar situation where high production costs are forcing producers to bring forward decommissioning plans forever shutting another source of oil supply even if prices recover to the point where production is profitable.

#### Conclusion

Looking back to 2016 from the future may indicate the year when the oil market began to fundamentally change.

The likely launch of a Chinese crude oil benchmark and China's entry in the SDR basket is a major crack in the US dollar hegemony over the crude oil market and also numerous commodities and political strength. After all, US sanctions against Iran and others would have been largely ineffective if Iran could fall back on another dominant currency to sell its natural resources.

After US and Europe raised sanctions against Russia over the annexation of the Crimea region, the pipeline deals struck with China and the oil and gas to be sold was already denominated in a mixture of renminbi and Russia's rouble.

The US central bank's plans to raise its federal funds rate and therefore the interest rate gradually in 2016 and the European Central Bank plans to loosen its monetary policy puts both banks in opposite paths as the US dollar will strengthen while the euro will weaken.

The ECB's fight against deflationary pressures is an attempt to inflate away its high levels of debt, but the fight will be ineffective since the crude oil oversupply is reducing global transportation costs and also the manufacturing cost base. The fight against deflation is really a fight against oil supply.

However, the above are just knowns and rarely a year has passed without some surprises in the oil market that could overturn the supply story to one of a shortage. Only time will tell.

After all, 2015 was the year when conflict in the Middle East increased, while oil prices fell, showing we are already in new territory.

By Kawai Wong (mailto:icisnews.europe@icis.com)

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## Biofuel needs \$70 oil to compete, says DuPont

Ed Crooks

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Advanced biofuel made from agricultural waste - the so called Holy Grail of the alternative energy industry - will not be competitive

with conventional fuel until the oil is back to \$70-\$80 per barrel, DuPont has said.

This prediction from the US chemicals group, which last week formally opened the world's largest cellulosic ethanol plant, underscores the challenge facing makers of "second-generation" biofuels. After a decade pursuing an elusive production process, companies are finding their business models threatened by the changing economics of the industry — as well as the politics of the US.

DuPont's new \$225m Iowa plant will, after some delay, begin making cellulosic ethanol next year, and the fuel is expected to result in 90 per cent fewer greenhouse gas emissions than conventional petrol.

Ethanol from the plant will be sold in California, which has mandated a 10 per cent reduction in the carbon intensity of transport fuels by 2020, through the addition of biofuels.

Jan Koninckx, DuPont's global head of biofuels, described the opening of the plant as a "historic day in technology". He said: "We're really reforming the transport energy sector . . . This is a phenomenal environmental benefit."

Using agricultural waste rather than fresh crops to make biofuel is difficult, though. At the plant DuPont will take corn waste left over from the harvest — leaves, husks, cobs and stalks, collectively known as "stover" — and turn its cellulose into ethanol. Other sources for cellulosic ethanol include bagasse, the waste cane left from sugar production, and specialist energy crops such as switchgrass.

Using waste as a feedstock in this way avoids many of the concerns raised by first-generation biofuels, particularly the worry that food production was being sacrificed to create fuel additives.

But the new cellulosic ethanol process needs advanced enzymes to release sugars held in the cellulose, and production levels in the US have been very low.

Only two plants are using this technology: one owned by Abengoa of Spain, and another that is a joint venture between Poet, the privately held ethanol producer, and Royal DSM, a Dutch technology company.

Both formally opened their plants a little over a year ago but, from January to September, only 1.65m gallons of cellulosic ethanol were produced in the US, according to the government's Environmental Protection Agency. That is 4 per cent of the volumes that the Poet and Abengoa plants were notionally capable of producing in that time.

DuPont claims to have a better understanding of the cellulosic ethanol production process. Nevertheless, Mr Koninckx acknowledged that the economics of cellulosic

#### 18/04/2016

### High-priced bioenergy

Cellulosic ethanol\* costs to compete with oil (\$ per barrel)



#### Biofuel needs \$70 oil to compete, says DuPont - FT.com

ethanol suggested it would not be competitive with oil-based fuels until the oil price had risen back above \$70 a barrel.

With oil priced at around \$50 now, it could easily rebound. But in the futures market Brent crude for delivery in December 2021 is trading at only \$65 per barrel — suggesting cellulosic ethanol will need some sort of official support for several years.

In the US, demand for ethanol is mandated under the Renewable Fuel Standard, a regulation requiring a specified volume of biofuels to be blended into transport and jet fuels and heating oil.

However, this regulation has come under attack from the oil industry, food producers and environmentalists — and the EPA has launched a new inquiry into ethanol's emissions.

Ethanol production has also been hitting what is known as the blend wall — the 10 per cent legal maximum for ethanol content in US car fuel.

Peder Holk Nielsen, chief executive of Novozymes, the Danish enzyme technology company that supplies DuPont rivals such as Beta Renewables in Italy, says the important issue is funding the industry's growth.

"The second wave of plants could be 20 or 30 or 200 or 2,000," he says. "But that will not happen unless investors understand that the plants will have access to the market . . . not just today, but in 2025."

To instil confidence, he says, the US administration needs to retain and extend the Renewable Fuel Standard. But many Republicans and some Democratic politicians have been arguing that it should be cut back or scrapped.

Robert Rapier, an energy analyst, says the problem with cellulosic ethanol is the difficulty in processing and logistically managing high volumes of the plant waste. "Technically it works," he says. "Economically it's a very difficult proposition."

But Mr Holk Neilsen of Novozymes argues that the environmental benefits deserve continued support. "Solutions do exist for many of the problems we face," he adds. "It's about the political courage to implement them."

Cellulosic ethanol seen as potential money spinner

Ellen Kullman, DuPont's chief executive for seven years until her retirement last month, identified cellulosic ethanol as one of the "tough" scientific challenges the group was taking on — and potentially an important source of future earnings growth.

However, Nelson Peltz, the activist investor whose Trian fund has taken a 2.7 per cent stake in DuPont, has attacked the company for its slow progress towards commercialising the technology, as part of his wider critique of its performance. Its commercial production of cellulosic ethanol had originally been scheduled to start last year.

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## IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation

## **Summary for Policymakers**

This Summary for Policymakers was formally approved at the 11th Session of Working Group III of the IPCC

Abu Dhabi, United Arab Emirates, 5-8 May 2011

## **Summary for Policy Makers**

#### **Coordinating Lead Authors:**

Ottmar Edenhofer (Germany), Ramon Pichs-Madruga (Cuba), Youba Sokona (Ethiopia/Mali), Kristin Seyboth (Germany/USA)

#### Lead Authors:

Dan Arvizu (USA), Thomas Bruckner (Germany), John Christensen (Denmark), Helena Chum (USA/Brazil) Jean-Michel Devernay (France), Andre Faaij (The Netherlands), Manfred Fischedick (Germany), Barry Goldstein (Australia), Gerrit Hansen (Germany), John Huckerby (New Zealand), Arnulf Jäger-Waldau (Italy/Germany), Susanne Kadner (Germany), Daniel Kammen (USA), Volker Krey (Austria/Germany), Arun Kumar (India), Anthony Lewis (Ireland), Oswaldo Lucon (Brazil), Patrick Matschoss (Germany), Lourdes Maurice (USA), Catherine Mitchell (United Kingdom), William Moomaw (USA), José Moreira (Brazil), Alain Nadai (France), Lars J. Nilsson (Sweden), John Nyboer (Canada), Atiq Rahman (Bangladesh), Jayant Sathaye (USA), Janet Sawin (USA), Roberto Schaeffer (Brazil), Tormod Schei (Norway), Steffen Schlömer (Germany), Ralph Sims (New Zealand), Christoph von Stechow (Germany), Aviel Verbruggen (Belgium), Kevin Urama (Kenya/Nigeria), Ryan Wiser (USA), Francis Yamba (Zambia), Timm Zwickel (Germany)

#### **Special Advisor:**

Jeffrey Logan (USA)

#### This chapter should be cited as:

IPCC, 2011: Summary for Policymakers. In: IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation [O. Edenhofer, R. Pichs-Madruga, Y. Sokona, K. Seyboth, P. Matschoss, S. Kadner, T. Zwickel, P. Eickemeier, G. Hansen, S. Schlömer, C. von Stechow (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

#### 1. Introduction

The Working Group III Special Report on Renewable Energy Sources and Climate Change Mitigation (SRREN) presents an assessment of the literature on the scientific, technological, environmental, economic and social aspects of the contribution of six renewable energy (RE) sources to the mitigation of climate change. It is intended to provide policy relevant information to governments, intergovernmental processes and other interested parties. This Summary for Policymakers provides an overview of the SRREN, summarizing the essential findings.

The SRREN consists of 11 chapters. Chapter 1 sets the context for RE and climate change; Chapters 2 through 7 provide information on six RE technologies, and Chapters 8 through 11 address integrative issues (see Figure SPM.1).



#### Figure SPM.1 | Structure of the SRREN. [Figure 1.1, 1.1.2]

References to chapters and sections are indicated with corresponding chapter and section numbers in square brackets. An explanation of terms, acronyms and chemical symbols used in this SPM can be found in the glossary of the SRREN (Annex I). Conventions and methodologies for determining costs, primary energy and other topics of analysis can be found in Annex II and Annex III. This report communicates uncertainty where relevant.<sup>1</sup>

#### 2. Renewable energy and climate change

*Demand for energy and associated services, to meet social and economic development and improve human welfare and health, is increasing.* All societies require energy services to meet basic human needs (e.g., lighting, cooking, space comfort, mobility and communication) and to serve productive processes. [1.1.1, 9.3.2] Since approximately 1850, global use of fossil fuels (coal, coal, coa

<sup>&</sup>lt;sup>1</sup> This report communicates uncertainty, for example, by showing the results of sensitivity analyses and by quantitatively presenting ranges in cost numbers as well as ranges in the scenario results. This report does not apply formal IPCC uncertainty terminology because at the time of the approval of this report, IPCC uncertainty guidance was in the process of being revised.

oil and gas) has increased to dominate energy supply, leading to a rapid growth in carbon dioxide  $(CO_2)$  emissions [Figure 1.6].

*Greenhouse gas (GHG) emissions resulting from the provision of energy services have contributed significantly to the historic increase in atmospheric GHG concentrations.* The IPCC Fourth Assessment Report (AR4) concluded that "Most of the observed increase in global average temperature since the mid-20th century is very likely<sup>2</sup> due to the observed increase in anthropogenic greenhouse gas concentrations."

*Recent data confirm that consumption of fossil fuels accounts for the majority of global anthropogenic GHG emissions.*<sup>3</sup> Emissions continue to grow and CO<sub>2</sub> concentrations had increased to over 390 ppm, or 39% above preindustrial levels, by the end of 2010. [1.1.1, 1.1.3]

*There are multiple options for lowering GHG emissions from the energy system while still satisfying the global demand for energy services.* [1.1.3, 10.1] Some of these possible options, such as energy conservation and efficiency, fossil fuel switching, RE, nuclear and carbon capture and storage (CCS) were assessed in the AR4. A comprehensive evaluation of any portfolio of mitigation options would involve an evaluation of their respective mitigation potential as well as their contribution to sustainable development and all associated risks and costs. [1.1.6] This report will concentrate on the role that the deployment of RE technologies can play within such a portfolio of mitigation options.

*As well as having a large potential to mitigate climate change, RE can provide wider benefits.* RE may, if implemented properly, contribute to social and economic development, energy access, a secure energy supply, and reducing negative impacts on the environment and health. [9.2, 9.3]

Under most conditions, increasing the share of RE in the energy mix will require policies to stimulate changes in the energy system. Deployment of RE technologies has increased rapidly in recent years, and their share is projected to increase substantially under most ambitious mitigation scenarios [1.1.5, 10.2]. Additional policies would be required to attract the necessary increases in investment in technologies and infrastructure [11.4.3, 11.5, 11.6.1, 11.7.5].

#### 3. Renewable energy technologies and markets

*RE comprises a heterogeneous class of technologies* (Box SPM.1). Various types of RE can supply electricity, thermal energy and mechanical energy, as well as produce fuels that are able to satisfy multiple energy service needs [1.2]. Some RE technologies can be deployed at the point of use (decentralized) in rural and urban environments, whereas others are primarily deployed within large (centralized) energy networks [1.2, 8.2, 8.3, 9.3.2]. Though a growing number of RE technologies are technically mature and are being deployed at significant scale, others are in an earlier phase of technical maturity and commercial deployment or fill specialized niche markets [1.2]. The energy output of RE technologies can be (i) variable and—to some degree— unpredictable over differing time scales (from minutes to years), (ii) variable but predictable, (iii) constant, or (iv) controllable [8.2, 8.3].

 $<sup>^{2}</sup>$  According to the formal uncertainty language used in the AR4, the term 'very likely' refers to a >90% assessed probability of occurrence.

<sup>&</sup>lt;sup>3</sup> The contributions of individual anthropogenic GHGs to total emissions in 2004, reported in AR4, expressed as  $CO_2eq$  were:  $CO_2$  from fossil fuels (56.6%),  $CO_2$  from deforestation, decay of biomass etc. (17.3%),  $CO_2$  from other (2.8%), methane (14.3%), nitrous oxide (7.9%) and fluorinated gases (1.1%) [Figure 1.1b, AR4, WG III, Chapter 1. For further information on sectoral emissions, including forestry, see also Figure 1.3b and associated footnotes.]

#### Box SPM.1 | Renewable energy sources and technologies considered in this report.

**Bioenergy** can be produced from a variety of biomass feedstocks, including forest, agricultural and livestock residues; short-rotation forest plantations; energy crops; the organic component of municipal solid waste; and other organic waste streams. Through a variety of processes, these feedstocks can be directly used to produce electricity or heat, or can be used to create gaseous, liquid, or solid fuels. The range of bioenergy technologies is broad and the technical maturity varies substantially. Some examples of commercially available technologies include small- and large-scale boilers, domestic pellet-based heating systems, and ethanol production from sugar and starch. Advanced biomass integrated gasification combined-cycle power plants and lignocellulose-based transport fuels are examples of technologies that are at a pre-commercial stage, while liquid biofuel production from algae and some other biological conversion approaches are at the research and development (R&D) phase. Bioenergy technologies have applications in centralized and decentralized settings, with the traditional use of biomass in developing countries being the most widespread current application.<sup>4</sup> Bioenergy typically offers constant or controllable output. Bioenergy projects usually depend on local and regional fuel supply availability, but recent developments show that solid biomass and liquid biofuels are increasingly traded internationally. [1.2, 2.1, 2.3, 2.6, 8.2, 8.3]

**Direct solar** energy technologies harness the energy of solar irradiance to produce electricity using photovoltaics (PV) and concentrating solar power (CSP), to produce thermal energy (heating or cooling, either through passive or active means), to meet direct lighting needs and, potentially, to produce fuels that might be used for transport and other purposes. The technology maturity of solar applications ranges from R&D (e.g., fuels produced from solar energy), to relatively mature (e.g., CSP), to mature (e.g., passive and active solar heating, and wafer-based silicon PV). Many but not all of the technologies are modular in nature, allowing their use in both centralized and decentralized energy systems. Solar energy is variable and, to some degree, unpredictable, though the temporal profile of solar energy output in some circumstances correlates relatively well with energy demands. Thermal energy storage offers the option to improve output control for some technologies such as CSP and direct solar heating. [1.2, 3.1, 3.3, 3.5, 3.7, 8.2, 8.3]

**Geothermal energy** utilizes the accessible thermal energy from the Earth's interior. Heat is extracted from geothermal reservoirs using wells or other means. Reservoirs that are naturally sufficiently hot and permeable are called hydrothermal reservoirs, whereas reservoirs that are sufficiently hot but that are improved with hydraulic stimulation are called enhanced geothermal systems (EGS). Once at the surface, fluids of various temperatures can be used to generate electricity or can be used more directly for applications that require thermal energy, including district heating or the use of lower-temperature heat from shallow wells for geothermal heat pumps used in heating or cooling applications. Hydrothermal power plants and thermal applications of geothermal energy are mature technologies, whereas EGS projects are in the demonstration and pilot phase while also undergoing R&D. When used to generate electricity, geothermal power plants typically offer constant output. [1.2, 4.1, 4.3, 8.2, 8.3]

**Hydropower** harnesses the energy of water moving from higher to lower elevations, primarily to generate electricity. Hydropower projects encompass dam projects with reservoirs, run-of-river and in-stream projects and cover a continuum in project scale. This variety gives hydropower the ability to meet large centralized urban needs as well as decentralized rural needs. Hydropower technologies are mature. Hydropower projects exploit a resource that varies temporally. However, the controllable output provided by hydropower facilities that have reservoirs can be used to meet peak electricity demands and help to balance electricity systems that have large amounts of variable RE

<sup>&</sup>lt;sup>4</sup> Traditional biomass is defined by the International Energy Agency (IEA) as biomass consumption in the residential sector in developing countries and refers to the often unsustainable use of wood, charcoal, agricultural residues, and animal dung for cooking and heating. All other biomass use is defined as modern [Annex I].

generation. The operation of hydropower reservoirs often reflects their multiple uses, for example, drinking water, irrigation, flood and drought control, and navigation, as well as energy supply. [1.2, 5.1, 5.3, 5.5, 5.10, 8.2]

**Ocean energy** derives from the potential, kinetic, thermal and chemical energy of seawater, which can be transformed to provide electricity, thermal energy, or potable water. A wide range of technologies are possible, such as barrages for tidal range, submarine turbines for tidal and ocean currents, heat exchangers for ocean thermal energy conversion, and a variety of devices to harness the energy of waves and salinity gradients. Ocean technologies, with the exception of tidal barrages, are at the demonstration and pilot project phases and many require additional R&D. Some of the technologies have variable energy output profiles with differing levels of predictability (e.g., wave, tidal range and current), while others may be capable of near-constant or even controllable operation (e.g., ocean thermal and salinity gradient). [1.2, 6.1, 6.2, 6.3, 6.4, 6.6, 8.2]

**Wind energy** harnesses the kinetic energy of moving air. The primary application of relevance to climate change mitigation is to produce electricity from large wind turbines located on land (onshore) or in sea- or freshwater (offshore). Onshore wind energy technologies are already being manufactured and deployed on a large scale. Offshore wind energy technologies have greater potential for continued technical advancement. Wind electricity is both variable and, to some degree, unpredictable, but experience and detailed studies from many regions have shown that the integration of wind energy generally poses no insurmountable technical barriers. [1.2, 7.1, 7.3, 7.5, 7.7, 8.2]

On a global basis, it is estimated that RE accounted for 12.9% of the total 492 Exajoules  $(EJ)^5$  of primary energy supply in 2008 (Box SPM.2 and Figure SPM.2). The largest RE contributor was biomass (10.2%), with the majority (roughly 60%) being traditional biomass used in cooking and heating applications in developing countries but with rapidly increasing use of modern biomass as well.<sup>6</sup> Hydropower represented 2.3%, whereas other RE sources accounted for 0.4%. [1.1.5] In 2008, RE contributed approximately 19% of global electricity supply (16% hydropower, 3% other RE) and biofuels contributed 2% of global road transport fuel supply. Traditional biomass (17%), modern biomass (8%), solar thermal and geothermal energy (2%) together fuelled 27% of the total global demand for heat. The contribution of RE to primary energy supply varies substantially by country and region. [1.1.5, 1.3.1, 8.1]

#### Box SPM.2 | Accounting for primary energy in the SRREN.

There is no single, unambiguous accounting method for calculating primary energy from noncombustible energy sources such as non-combustible RE sources and nuclear energy. The SRREN adopts the 'direct equivalent' method for accounting for primary energy supply. In this method, fossil fuels and bioenergy are accounted for based on their heating value while non-combustible energy sources, including nuclear energy and all non-combustible RE, are accounted for based on the secondary energy that they produce. This may lead to an understatement of the contribution of non-combustible RE and nuclear compared to bioenergy and fossil fuels by a factor of roughly 1.2 up to 3. The selection of the accounting method also impacts the relative shares of different individual energy sources. Comparisons in the data and figures presented in the SRREN between fossil fuels and bioenergy on the one hand, and non-combustible RE and nuclear energy on the other, reflect this accounting method. [1.1.9, Annex II.4]

<sup>&</sup>lt;sup>5</sup> 1 Exajoule =  $10^{18}$  joules = 23.88 million tonnes of oil equivalent (Mtoe).

<sup>&</sup>lt;sup>6</sup> In addition to this 60% share of traditional biomass, there is biomass use estimated to amount to 20 to 40% not reported in official primary energy databases, such as dung, unaccounted production of charcoal, illegal logging, fuelwood gathering, and agricultural residue use. [2.1, 2.5]



**Figure SPM.2** | Shares of energy sources in total global primary energy supply in 2008 (492 EJ). Modern biomass contributes 38% of the total biomass share. [Figure 1.10, 1.1.5] Notes: Underlying data for figure have been converted to the 'direct equivalent' method of accounting for primary energy supply. [Box SPM.2, 1.1.9, Annex II.4]

**Deployment of RE has been increasing rapidly in recent years** (Figure SPM.3). Various types of government policies, the declining cost of many RE technologies, changes in the prices of fossil fuels, an increase of energy demand and other factors have encouraged the continuing increase in the use of RE. [1.1.5, 9.3, 10.5, 11.2, 11.3] Despite global financial challenges, RE capacity continued to grow rapidly in 2009 compared to the cumulative installed capacity from the previous year, including wind power (32% increase, 38 Gigawatts (GW) added), hydropower (3%, 31 GW added), grid-connected photovoltaics (53%, 7.5 GW added), geothermal power (4%, 0.4 GW added), and solar hot water/heating (21%, 31 GW<sub>th</sub> added). Biofuels accounted for 2% of global road transport fuel demand in 2008 and nearly 3% in 2009. The annual production of ethanol increased to 1.6 EJ (76 billion litres) by the end of 2009 and biodiesel to 0.6 EJ (17 billion litres). [1.1.5, 2.4, 3.4, 4.4, 5.4, 7.4]

Of the approximate 300 GW of new electricity generating capacity added globally over the twoyear period from 2008 to 2009, 140 GW came from RE additions. Collectively, developing countries host 53% of global RE electricity generation capacity [1.1.5]. At the end of 2009, the use of RE in hot water/heating markets included modern biomass (270 GW<sub>th</sub>), solar (180 GW<sub>th</sub>), and geothermal (60 GW<sub>th</sub>). The use of decentralized RE (excluding traditional biomass) in meeting rural energy needs at the household or village level has also increased, including hydropower stations, various modern biomass options, PV, wind or hybrid systems that combine multiple technologies. [1.1.5, 2.4, 3.4, 4.4, 5.4]



**Figure SPM.3** | Historical development of global primary energy supply from renewable energy from 1971 to 2008 [Figure 1.12, 1.1.5].

Notes: Technologies are referenced to separate vertical units for display purposes only. Underlying data for figure has been converted to the 'direct equivalent' method of accounting for primary energy supply [Box SPM.2, 1.1.9, Annex II.4], except that the energy content of biofuels is reported in secondary energy terms (the primary biomass used to produce the biofuel would be higher due to conversion losses [2.3, 2.4]).

*The global technical potential*<sup>7</sup> *of RE sources will not limit continued growth in the use of RE.* A wide range of estimates is provided in the literature, but studies have consistently found that the total global technical potential for RE is substantially higher than global energy demand (Figure SPM.4) [1.2.2, 10.3, Annex II]. The technical potential for solar energy is the highest among the RE sources, but substantial technical potential exists for all six RE sources. Even in regions with relatively low levels of technical potential for any individual RE source, there are typically

<sup>&</sup>lt;sup>7</sup> Definitions of technical potential often vary by study. 'Technical potential' is used in the SRREN as the amount of RE output obtainable by full implementation of demonstrated technologies or practices. No explicit reference to costs, barriers or policies is made. Technical potentials reported in the literature and assessed in the SRREN, however, may have taken into account practical constraints and when explicitly stated they are generally indicated in the underlying report. [Annex I]

significant opportunities for increased deployment compared to current levels. [1.2.2, 2.2, 2.8, 3.2, 4.2, 5.2, 6.2, 6.4, 7.2, 8.2, 8.3, 10.3] In the longer term and at higher deployment levels, however, technical potentials indicate a limit to the contribution of some individual RE technologies. Factors such as sustainability concerns [9.3], public acceptance [9.5], system integration and infrastructure constraints [8.2], or economic factors [10.3] may also limit deployment of RE technologies.



# **Figure SPM.4** | Ranges of global technical potentials of RE sources derived from studies presented in Chapters 2 through 7. Biomass and solar are shown as primary energy due to their multiple uses; note that the figure is presented in logarithmic scale due to the wide range of assessed data [Figure 1.17, 1.2.3].

Notes: Technical potentials reported here represent total worldwide potentials for annual RE supply and do not deduct any potential that is already being utilized. Note that RE electricity sources could also be used for heating applications, whereas biomass and solar resources are reported only in primary energy terms but could be used to meet various energy service needs. Ranges are based on various methods and apply to different future years; consequently, the resulting ranges are not strictly comparable across technologies. For the data behind Figure SPM.4 and additional notes that apply, see Chapter 1 Annex, Table A.1.1 (as well as the underlying chapters).

### Climate change will have impacts on the size and geographic distribution of the technical potential for RE sources, but research into the magnitude of these possible effects is nascent.

Because RE sources are, in many cases, dependent on the climate, global climate change will affect the RE resource base, though the precise nature and magnitude of these impacts is uncertain. The future technical potential for bioenergy could be influenced by climate change through impacts on biomass production such as altered soil conditions, precipitation, crop productivity and other factors. The overall impact of a global mean temperature change of less than 2°C on the technical potential of bioenergy is expected to be relatively small on a global basis. However, considerable regional differences could be expected and uncertainties are larger and more difficult to assess compared to other RE options due to the large number of feedback mechanisms involved. [2.2, 2.6] For solar energy, though climate change is expected to influence the distribution and variability of cloud cover, the impact of these changes on overall technical potential is expected to be small [3.2]. For hydropower the overall impacts on the global technical potential is expected to be slightly positive. However, results also indicate the possibility of substantial variations across regions and even within countries. [5.2] Research to date suggests that climate change is not expected to greatly impact the global technical potential for wind energy development but changes in the regional distribution of the wind energy resource may be expected [7.2]. Climate change is not anticipated to have significant impacts on the size or geographic distribution of geothermal or ocean energy resources [4.2, 6.2].

*The levelized cost of energy*<sup>8</sup> *for many RE technologies is currently higher than existing energy prices, though in various settings RE is already economically competitive.* Ranges of recent levelized costs of energy for selected commercially available RE technologies are wide, depending on a number of factors including, but not limited to, technology characteristics, regional variations in cost and performance, and differing discount rates (Figure SPM.5). [1.3.2, 2.3, 2.7, 3.8, 4.8, 5.8, 6.7, 7.8, 10.5, Annex III] Some RE technologies are broadly competitive with existing market energy prices. Many of the other RE technologies can provide competitive energy services in certain circumstances, for example, in regions with favourable resource conditions or that lack the infrastructure for other low-cost energy supplies. In most regions of the world, policy measures are still required to ensure rapid deployment of many RE sources. [2.3, 2.7, 3.8, 4.7, 5.8, 6.7, 7.8, 10.5]

Monetizing the external costs of energy supply would improve the relative competitiveness of RE. The same applies if market prices increase due to other reasons (Figure SPM.5). [10.6] The levelized cost of energy for a technology is not the sole determinant of its value or economic competitiveness. The attractiveness of a specific energy supply option depends also on broader economic as well as environmental and social aspects, and the contribution that the technology provides to meeting specific energy services (e.g., peak electricity demands) or imposes in the form of ancillary costs on the energy system (e.g., the costs of integration). [8.2, 9.3, 10.6]

<sup>&</sup>lt;sup>8</sup> The levelized cost of energy represents the cost of an energy generating system over its lifetime; it is calculated as the per-unit price at which energy must be generated from a specific source over its lifetime to break even. It usually includes all private costs that accrue upstream in the value chain, but does not include the downstream cost of delivery to the final customer; the cost of integration, or external environmental or other costs. Subsidies and tax credits are also not included.



**Figure SPM.5** | Range in recent levelized cost of energy for selected commercially available RE technologies in comparison to recent non-renewable energy costs. Technology subcategories and discount rates were aggregated for this figure. For related figures with less or no such aggregation, see [1.3.2, 10.5, Annex III].

The cost of most RE technologies has declined and additional expected technical advances would result in further cost reductions. Significant advances in RE technologies and associated long-term cost reductions have been demonstrated over the last decades, though periods of rising prices have sometimes been experienced (due to, for example, increasing demand for RE in excess of available supply) (Figure SPM.6). The contribution of different drivers (e.g., R&D, economies of scale, deployment-oriented learning, and increased market competition among RE suppliers) is not always understood in detail. [2.7, 3.8, 7.8, 10.5] Further cost reductions are expected, resulting in greater potential deployment and consequent climate change mitigation. Examples of important areas of potential technological advancement include: new and improved feedstock production and supply systems, biofuels produced via new processes (also called next-generation or advanced biofuels, e.g., lignocellulosic) and advanced biorefining [2.6]; advanced PV and CSP technologies and manufacturing processes [3.7]; enhanced geothermal systems (EGS) [4.6]; multiple emerging ocean technologies [6.6]; and foundation and turbine designs for offshore wind energy [7.7]. Further cost reductions for hydropower are expected to be less significant than some of the other RE technologies, but R&D opportunities exist to make hydropower projects technically feasible in a wider range of locations and to improve the technical performance of new and existing projects [5.3, 5.7, 5.8].



**Figure SPM.6** | Selected experience curves in logarithmic scale for (a) the price of silicon PV modules and onshore wind power plants per unit of capacity; and (b) the cost of sugarcane-based ethanol production [data from Figure 3.17, 3.8.3, Figure 7.20, 7.8.2, Figure 2.21, 2.7.2].

Notes: Depending on the setting, cost reductions may occur at various geographic scales. The country-level examples provided here derive from the published literature. No global dataset of wind power plant prices or costs is readily available. Reductions in the cost or price of a technology per unit of capacity understate reductions in the levelized cost of energy of that technology when performance improvements occur [7.8.4, 10.5].

A variety of technology-specific challenges (in addition to cost) may need to be addressed to enable RE to significantly upscale its contribution to reducing GHG emissions. For the increased and sustainable use of bioenergy, proper design, implementation and monitoring of sustainability frameworks can minimize negative impacts and maximize benefits with regard to social, economic and environmental issues [SPM.5, 2.2, 2.5, 2.8]. For solar energy, regulatory and institutional barriers can impede deployment, as can integration and transmission issues [3.9]. For geothermal energy, an important challenge would be to prove that enhanced geothermal systems (EGS) can be deployed economically, sustainably and widely [4.5, 4.6, 4.7, 4.8]. New hydropower projects can have ecological and social impacts that are very site specific, and increased deployment may require improved sustainability assessment tools, and regional and multi-party collaborations to address energy and water needs [5.6, 5.9, 5.10]. The deployment of ocean energy could benefit from testing centres for demonstration projects, and from dedicated policies and regulations that encourage early deployment [6.4]. For wind energy, technical and institutional solutions to transmission constraints and operational integration concerns may be especially important, as might public acceptance issues relating primarily to landscape impacts [7.5, 7.6, 7.9].

#### 4. Integration into present and future energy systems

Various RE resources are already being successfully integrated into energy supply systems [8.2] and into end-use sectors [8.3] (Figure SPM.7).



**Figure SPM.7** | Pathways for RE integration to provide energy services, either into energy supply systems or on-site for use by the end-use sectors. [Figure 8.1, 8.1]

*The characteristics of different RE sources can influence the scale of the integration challenge.* Some RE resources are widely distributed geographically. Others, such as large-scale hydropower, can be more centralized but have integration options constrained by geographic location. Some RE resources are variable with limited predictability. Some have lower physical energy densities and different technical specifications from fossil fuels. Such characteristics can constrain ease of integration and invoke additional system costs particularly when reaching higher shares of RE. [8.2] Integrating RE into most existing energy supply systems and end-use sectors at an accelerated rate—leading to higher shares of RE—is technologically feasible, though will result in a number of additional challenges. Increased shares of RE are expected within an overall portfolio of low GHG emission technologies [10.3, Tables 10.4-10.6]. Whether for electricity, heating, cooling, gaseous fuels or liquid fuels, including integration directly into end-use sectors, the RE integration challenges are contextual and site specific and include the adjustment of existing energy supply systems [8.2, 8.3].

## The costs and challenges of integrating increasing shares of RE into an existing energy supply system depend on the current share of RE, the availability and characteristics of RE resources, the system characteristics, and how the system evolves and develops in the future.

• RE can be integrated into all types of *electricity* systems, from large inter-connected continental-scale grids [8.2.1] down to small stand-alone systems and individual buildings [8.2.5]. Relevant system characteristics include the generation mix and its flexibility, network infrastructure, energy market designs and institutional rules, demand location, demand profiles, and control and communication capability. Wind, solar PV energy and CSP without storage can be more difficult to integrate than dispatchable<sup>9</sup> hydropower, bioenergy, CSP with storage and geothermal energy.

As the penetration of variable RE sources increases, maintaining system reliability may become more challenging and costly. Having a portfolio of complementary RE technologies is one solution to reduce the risks and costs of RE integration. Other solutions include the development of complementary flexible generation and the more flexible operation of existing schemes; improved short-term forecasting, system operation and planning tools; electricity demand that can respond in relation to supply availability; energy storage technologies (including storage-based hydropower); and modified institutional arrangements. Electricity network transmission (including interconnections between systems) and/or distribution infrastructure may need to be strengthened and extended, partly because of the geographical distribution and fixed remote locations of many RE resources. [8.2.1]

- *District heating systems* can use low-temperature thermal RE inputs such as solar and geothermal heat, or biomass, including sources with few competing uses such as refusederived fuels. *District cooling* can make use of cold natural waterways. Thermal storage capability and flexible cogeneration can overcome supply and demand variability challenges as well as provide demand response for electricity systems. [8.2.2]
- In *gas distribution grids*, injecting biomethane, or in the future, RE-derived hydrogen and synthetic natural gas, can be achieved for a range of applications but successful integration requires that appropriate gas quality standards are met and pipelines upgraded where necessary [8.2.3].
- *Liquid fuel systems* can integrate biofuels for transport applications or for cooking and heating applications. Pure (100%) biofuels, or more usually those blended with petroleum-based fuels, usually need to meet technical standards consistent with vehicle engine fuel specifications. [8.2.4, 8.3.1]

<sup>&</sup>lt;sup>9</sup> Electricity plants that can schedule power generation as and when required are classed as dispatchable [8.2.1.1, Annex I]. Variable RE technologies are partially dispatchable (i.e., only when the RE resource is available). CSP plants are classified as dispatchable when heat is stored for use at night or during periods of low sunshine.

## There are multiple pathways for increasing the shares of RE across all end-use sectors. The ease of integration varies depending on region, characteristics specific to the sector and the technology.

- For *transport*, liquid and gaseous biofuels are already and are expected to continue to be integrated into the fuel supply systems of a growing number of countries. Integration options may include decentralized on-site or centralized production of RE hydrogen for fuel cell vehicles and RE electricity for rail and electric vehicles [8.2.1, 8.2.3] depending on infrastructure and vehicle technology developments [8.3.1]. Future demand for electric vehicles could also enhance flexible electricity generation systems [8.2.1, 8.3.1].
- In the *building* sector, RE technologies can be integrated into both new and existing structures to produce electricity, heating and cooling. Supply of surplus energy may be possible, particularly for energy efficient building designs [8.3.2]. In developing countries, the integration of RE supply systems is feasible for even modest dwellings [8.3.2, 9.3.2].
- Agriculture as well as food and fibre process *industries* often use biomass to meet direct heat and power demands on-site. They can also be net exporters of surplus fuels, heat, and electricity to adjacent supply systems [8.3.3, 8.3.4]. Increasing the integration of RE for use by industries is an option in several sub-sectors, for example through electro-thermal technologies or, in the longer term, by using RE hydrogen [8.3.3].

The costs associated with RE integration, whether for electricity, heating, cooling, gaseous or liquid fuels, are contextual, site-specific and generally difficult to determine. They may include additional costs for network infrastructure investment, system operation and losses, and other adjustments to the existing energy supply systems as needed. The available literature on integration costs is sparse and estimates are often lacking or vary widely.

*In order to accommodate high RE shares, energy systems will need to evolve and be adapted [8.2, 8.3].* Long-term integration efforts could include investment in enabling infrastructure; modification of institutional and governance frameworks; attention to social aspects, markets and planning; and capacity building in anticipation of RE growth [8.2, 8.3]. Furthermore, integration of less mature technologies, including biofuels produced through new processes (also called advanced biofuels or next-generation biofuels), fuels generated from solar energy, solar cooling, ocean energy technologies, fuel cells and electric vehicles, will require continuing investments in research, development and demonstration (RD&D), capacity building and other supporting measures [2.6, 3.7, 11.5, 11.6, 11.7].

RE could shape future energy supply and end-use systems, in particular for electricity, which is expected to attain higher shares of RE earlier than either the heat or transport fuel sectors at the global level [10.3]. Parallel developments in electric vehicles [8.3.1], increased heating and cooling using electricity (including heat pumps) [8.2.2, 8.3.2, 8.3.3], flexible demand response services (including the use of smart meters) [8.2.1], energy storage and other technologies could be associated with this trend.

As infrastructure and energy systems develop, in spite of the complexities, there are few, if any, fundamental technological limits to integrating a portfolio of RE technologies to meet a majority share of total energy demand in locations where suitable RE resources exist or can be supplied. However, the actual rate of integration and the resulting shares of RE will be influenced by factors such as costs, policies, environmental issues and social aspects. [8.2, 8.3, 9.3, 9.4, 10.2, 10.5]

#### 5. Renewable energy and sustainable development

*Historically, economic development has been strongly correlated with increasing energy use and growth of GHG emissions, and RE can help decouple that correlation, contributing to sustainable development (SD).* Though the exact contribution of RE to SD has to be evaluated in a country-specific context, RE offers the opportunity to contribute to social and economic development, energy access, secure energy supply, climate change mitigation, and the reduction of negative environmental and health impacts. [9.2] Providing access to modern energy services would support the achievement of the Millennium Development Goals. [9.2.2, 9.3.2]

- *RE can contribute to social and economic development.* Under favorable conditions, cost savings in comparison to non-RE use exist, in particular in remote and in poor rural areas lacking centralized energy access. [9.3.1, 9.3.2.] Costs associated with energy imports can often be reduced through the deployment of domestic RE technologies that are already competitive [9.3.3]. RE can have a positive impact on job creation although the studies available differ with respect to the magnitude of net employment [9.3.1].
- *RE can help accelerate access to energy, particularly for the 1.4 billion people without access to electricity and the additional 1.3 billion using traditional biomass.* Basic levels of access to modern energy services can provide significant benefits to a community or household. In many developing countries, decentralized grids based on RE and the inclusion of RE in centralized energy grids have expanded and improved energy access. In addition, non-electrical RE technologies also offer opportunities for modernization of energy services, for example, using solar energy for water heating and crop drying, biofuels for transportation, biogas and modern biomass for heating, cooling, cooking and lighting, and wind for water pumping. [9.3.2, 8.1] The number of people without access to modern energy services is expected to remain unchanged unless relevant domestic policies are implemented, which may be supported or complemented by international assistance as appropriate. [9.3.2, 9.4.2]
- *RE options can contribute to a more secure energy supply, although specific challenges for integration must be considered.* RE deployment might reduce vulnerability to supply disruption and market volatility if competition is increased and energy sources are diversified. [9.3.3, 9.4.3] Scenario studies indicate that concerns regarding secure energy supply could continue in the future without technological improvements within the transport sector [2.8, 9.4.1.1, 9.4.3.1, 10.3]. The variable output profiles of some RE technologies often necessitate technical and institutional measures appropriate to local conditions to assure energy supply reliability [8.2, 9.3.3].
- In addition to reduced GHG emissions, RE technologies can provide other important environmental benefits. Maximizing these benefits depends on the specific technology, management, and site characteristics associated with each RE project.
  - Lifecycle assessments (LCA) for electricity generation indicate that GHG emissions from RE technologies are, in general, significantly lower than those associated with fossil fuel options, and in a range of conditions, less than fossil fuels employing CCS. The median values for all RE range from 4 to 46 g CO<sub>2</sub>eq/kWh while those for fossil fuels range from 469 to 1,001 g CO<sub>2</sub>eq/kWh (excluding land use change emissions) (Figure SPM 8).
  - Most current bioenergy systems, including liquid biofuels, result in GHG emission reductions, and most biofuels produced through new processes (also called advanced biofuels or next-generation biofuels) could provide higher GHG mitigation. The GHG balance may be affected by land use changes and corresponding emissions and removals. Bioenergy can lead to avoided GHG

emissions from residues and wastes in landfill disposals and co-products; the combination of bioenergy with CCS may provide for further reductions (see Figure SPM 8). The GHG implications related to land management and land use changes in carbon stocks have considerable uncertainties. [2.2, 2.5, 9.3.4.1]

The sustainability of bioenergy, in particular in terms of lifecycle GHG emissions, is influenced by land and biomass resource management practices. Changes in land and forest use or management that, according to a considerable number of studies, could be brought about *directly* or *indirectly* by biomass production for use as fuels, power or heat, can decrease or increase terrestrial carbon stocks. The same studies also show that indirect changes in terrestrial carbon stocks have considerable uncertainties, are not directly observable, are complex to model and are difficult to attribute to a single cause. Proper governance of land use, zoning, and choice of biomass production systems are key considerations for policy makers [2.4.5, 2.5.1, 9.3.4, 9.4.4]. Policies are in place that aim to ensure that the benefits from bioenergy, such as rural development, overall improvement of agricultural management and the contribution to climate change mitigation, are realized; their effectiveness has not been assessed. [2.2, 2.5, 2.8]



Count of Estimates	222(+4)	124	42	8	28	10	126	125	83(+7)	24	169(+12)
Count of References	52(+0)	26	13	6	11	5	49	32	36(+4)	10	50(+10)

**Figure SPM.8.** | Estimates of lifecycle GHG emissions (g  $CO_2eq/kWh$ ) for broad categories of electricity generation technologies, plus some technologies integrated with CCS. Land use-related net changes in carbon stocks (mainly applicable to biopower and hydropower from reservoirs) and

land management impacts are excluded; negative estimates<sup>10</sup> for biopower are based on assumptions about avoided emissions from residues and wastes in landfill disposals and coproducts. References and methods for the review are reported in Annex II. The number of estimates is greater than the number of references because many studies considered multiple scenarios. Numbers reported in parentheses pertain to additional references and estimates that evaluated technologies with CCS. Distributional information relates to estimates currently available in LCA literature, not necessarily to underlying theoretical or practical extrema, or the true central tendency when considering all deployment conditions. [Figure 9.8, 9.3.4.1]

- *RE technologies, in particular non-combustion based options, can offer benefits with respect to air pollution and related health concerns* [9.3.4.3, 9.4.4.1]. Improving traditional biomass use can significantly reduce local and indoor air pollution (alongside GHG emissions, deforestation and forest degradation) and lower associated health impacts, particularly for women and children in developing countries [2.5.4, 9.3.4.4].
- *Water availability could influence choice of RE technology.* Conventional watercooled thermal power plants may be especially vulnerable to conditions of water scarcity and climate change. In areas where water scarcity is already a concern, nonthermal RE technologies or thermal RE technologies using dry cooling can provide energy services without additional stress on water resources. Hydropower and some bioenergy systems are dependent on water availability, and can either increase competition or mitigate water scarcity. Many impacts can be mitigated by siting considerations and integrated planning. [2.5.5.1, 5.10, 9.3.4.4]
- Site-specific conditions will determine the degree to which RE technologies impact biodiversity. RE-specific impacts on biodiversity may be positive or negative. [2.5, 3.6, 4.5, 5.6, 6.5, , 9.3.4.6]
- *RE technologies have low fatality rates.* Accident risks of RE technologies are not negligible, but their often decentralized structure strongly limits the potential for disastrous consequences in terms of fatalities. However, dams associated with some hydropower projects may create a specific risk depending on site-specific factors. [9.3.4.7]

#### 6. Mitigation potentials and costs

A significant increase in the deployment of RE by 2030, 2050 and beyond is indicated in the majority of the 164 scenarios reviewed in this Special Report.<sup>11</sup> In 2008, total RE production was roughly 64 EJ/yr (12.9% of total primary energy supply) with more than 30 EJ/yr of this being traditional biomass. More than 50% of the scenarios project levels of RE deployment in 2050 of more than 173 EJ/yr reaching up to over 400 EJ/yr in some cases (Figure SPM.9). Given that traditional biomass use decreases in most scenarios, a corresponding increase in the production level of RE (excluding traditional biomass) anywhere from roughly three-fold to more than ten-fold is projected. The global primary energy supply share of RE differs substantially among the

<sup>&</sup>lt;sup>10</sup> 'Negative estimates' within the terminology of lifecycle assessments presented in the SRREN refer to avoided emissions. Unlike the case of bioenergy combined with CCS, avoided emissions do not remove GHGs from the atmosphere.

<sup>&</sup>lt;sup>11</sup> For this purpose a review of 164 global scenarios from 16 different large-scale integrated models was conducted. Although the set of scenarios allows for a meaningful assessment of uncertainty, the reviewed 164 scenarios do not represent a fully random sample suitable for rigorous statistical analysis and do not represent always the full RE portfolio (e.g., so far ocean energy is only considered in a few scenarios) [10.2.2]. For more specific analysis, a subset of 4 illustrative scenarios from the set of 164 was used. They represent a span from a baseline scenario without specific mitigation targets to three scenarios representing different  $CO_2$  stabilization levels. [10.3]

scenarios. More than half of the scenarios show a contribution from RE in excess of a 17% share of primary energy supply in 2030 rising to more than 27% in 2050. The scenarios with the highest RE shares reach approximately 43% in 2030 and 77% in 2050. [10.2, 10.3]

**RE** can be expected to expand even under baseline scenarios. Most baseline scenarios show RE deployments significantly above the 2008 level of 64 EJ/yr and up to 120 EJ/yr by 2030. By 2050, many baseline scenarios reach RE deployment levels of more than 100 EJ/yr and in some cases up to about 250 EJ/yr (Figure SPM.9). These baseline deployment levels result from a range of assumptions, including, for example, continued demand growth for energy services throughout the century, the ability of RE to contribute to increased energy access and the limited long-term availability of fossil resources. Other assumptions (e.g., improved costs and performance of RE technologies) render RE technologies increasingly economically competitive in many applications even in the absence of climate policy. [10.2]

*RE deployment significantly increases in scenarios with low GHG stabilization concentrations.* Low GHG stabilization scenarios lead on average to higher RE deployment compared to the baseline. However, for any given long-term GHG concentration goal, the scenarios exhibit a wide range of RE deployment levels (Figure SPM.9). In scenarios that stabilize the atmospheric CO<sub>2</sub> concentrations at a level of less than 440 ppm, the median RE deployment level in 2050 is 248 EJ/yr (139 in 2030), with the highest levels reaching 428 EJ/yr by 2050 (252 in 2030). [10.2]



**Figure SPM.9** | Global RE primary energy supply (direct equivalent) from 164 long-term scenarios versus fossil and industrial  $CO_2$  emissions in 2030 and 2050. Colour coding is based on categories of atmospheric  $CO_2$  concentration stabilization levels that are defined consistently with those in the AR4. The panels to the right of the scatterplots show the deployment levels of RE in each of the atmospheric  $CO_2$  concentration categories. The thick black line corresponds to the median, the coloured box corresponds to the inter-quartile range (25th to 75th percentile) and the ends of the white surrounding bars correspond to the total range across all reviewed scenarios. The grey crossed lines show the relationship in 2007. [Figure 10.2, 10.2.2.2]

Notes: For data reporting reasons only 161 scenarios are included in the 2030 results shown here, as opposed to the full set of 164 scenarios. RE deployment levels below those of today are a result of model output and differences in the reporting of traditional biomass. For details on the use of the 'direct equivalent' method of accounting for primary energy supply and the implied care needed in the interpretation of scenario results, see Box SPM.2. Note that categories V and above are not included and category IV is extended to 600 ppm from 570 ppm, because all stabilization scenarios lie below 600 ppm  $CO_2$  in 2100 and because the lowest baseline scenarios reach concentration levels of slightly more than 600 ppm by 2100.

Many combinations of low-carbon energy supply options and energy efficiency improvements can contribute to given low GHG concentration levels, with RE becoming the dominant low-carbon energy supply option by 2050 in the majority of scenarios. This wide range of results originates in assumptions about factors such as developments in RE technologies (including bioenergy with CCS) and their associated resource bases and costs; the comparative attractiveness of other mitigation options (e.g., end-use energy efficiency, nuclear energy, fossil energy with CCS); patterns of consumption and production; fundamental drivers of energy services demand (including future population and economic growth); the ability to integrate variable RE sources into power grids; fossil fuel resources; specific policy approaches to mitigation; and emissions trajectories towards long-term concentration levels. [10.2]

The scenario review in this Special Report indicates that RE has a large potential to mitigate GHG emissions. Four illustrative scenarios span a range of global cumulative  $CO_2$  savings between 2010 and 2050, from about 220 to 560 Gt  $CO_2$  compared to about 1,530 Gt cumulative fossil and industrial  $CO_2$  emissions in the IEA World Energy Outlook 2009 Reference Scenario during the same period. The precise attribution of mitigation potentials to RE depends on the role scenarios attribute to specific mitigation technologies, on complex system behaviours and, in particular, on the energy sources that RE displaces. Therefore, attribution of precise mitigation potentials to RE should be viewed with appropriate caution. [10.2, 10.3, 10.4]

*Scenarios generally indicate that growth in RE will be widespread around the world.* Although the precise distribution of RE deployment among regions varies substantially across scenarios, the scenarios are largely consistent in indicating widespread growth in RE deployment around the globe. In addition, the total RE deployment is higher over the long term in the group of non-Annex I countries<sup>12</sup> than in the group of Annex I countries in most scenarios (Figure SPM.10). [10.2, 10.3]



Figure SPM.10. | Global RE primary energy supply (direct equivalent) by source in the group of Annex I (AI) and the group of Non-Annex I (NAI) countries in 164 long-term scenarios by 2030 and

<sup>&</sup>lt;sup>12</sup> The terms 'Annex I' and 'non-Annex I' are categories of countries that derive from the United Nations Framework Convention on Climate Change (UNFCCC).

2050. The thick black line corresponds to the median, the coloured box corresponds to the interquartile range (25th to 75th percentile) and the ends of the white surrounding bars correspond to the total range across all reviewed scenarios. [Figure 10.8, 10.2.2.5]

Notes: For details on the use of the 'direct equivalent' method of accounting for primary energy supply and the implied care needed in the interpretation of scenario results, see Box SPM.2. More specifically, the ranges of secondary energy provided from bioenergy, wind energy and direct solar energy can be considered of comparable magnitude in their higher penetration scenarios in 2050. Ocean energy is not presented here as only very few scenarios consider this RE technology.

Scenarios do not indicate an obvious single dominant RE technology at a global level; in addition, the global overall technical potentials do not constrain the future contribution of RE. Although the contribution of RE technologies varies across scenarios, modern biomass, wind and direct solar commonly make up the largest contributions of RE technologies to the energy system by 2050 (Figure SPM.11). All scenarios assessed confirm that technical potentials will not be the limiting factors for the expansion of RE at a global scale. Despite significant technological and regional differences, in the four illustrative scenarios less than 2.5% of the global available technical RE potential is used. [10.2, 10.3]



Bioenergy Supply is Accounted for Prior to Conversion

Primary Energy Supply is Accounted for Based on Secondary Energy Produced

**Figure SPM.11.** | Global primary energy supply (direct equivalent) of bioenergy, wind, direct solar, hydro, and geothermal energy in 164 long-term scenarios in 2030 and 2050, and grouped by different categories of atmospheric CO<sub>2</sub> concentration level that are defined consistently with those in the AR4. The thick black line corresponds to the median, the coloured box corresponds to the inter-quartile range (25th to 75th percentile) and the ends of the white surrounding bars correspond to the total range across all reviewed scenarios. [Excerpt from Figure 10.9, 10.2.2.5]

Notes: For details on the use of the 'direct equivalent' method of accounting for primary energy supply and the implied care needed in the interpretation of scenario results, see Box SPM.2. More specifically, the ranges of secondary energy

provided from bioenergy, wind energy and direct solar energy can be considered of comparable magnitude in their higher penetration scenarios in 2050. Ocean energy is not presented here as only very few scenarios consider this RE technology. Note that categories V and above are not included and category IV is extended to 600 ppm from 570 ppm, because all stabilization scenarios lie below 600 ppm  $CO_2$  in 2100 and because the lowest baselines scenarios reach concentration levels of slightly more than 600 ppm by 2100.

*Individual studies indicate that if RE deployment is limited, mitigation costs increase and low GHG concentration stabilizations may not be achieved.* A number of studies have pursued scenario sensitivities that assume constraints on the deployment of individual mitigation options, including RE as well as nuclear and fossil energy with CCS. There is little agreement on the precise magnitude of the cost increase. [10.2]

A transition to a low-GHG economy with higher shares of RE would imply increasing investments in technologies and infrastructure. The four illustrative scenarios analyzed in detail in the SRREN estimate global cumulative RE investments (in the power generation sector only) ranging from  $USD_{2005}$  1,360 to 5,100 billion for the decade 2011 to 2020, and from  $USD_{2005}$  1,490 to 7,180 billion for the decade 2021 to 2030. The lower values refer to the IEA World Energy Outlook 2009 Reference Scenario and the higher ones to a scenario that seeks to stabilize atmospheric  $CO_2$  (only) concentration at 450 ppm. The annual averages of these investment needs are all smaller than 1% of the world's gross domestic product (GDP). Beyond differences in the design of the models used to investigate these scenarios, the range can be explained mainly by differences in GHG concentrations assessed and constraints imposed on the set of admissible mitigation technologies. Increasing the installed capacity of RE power plants will reduce the amount of fossil and nuclear fuels that otherwise would be needed in order to meet a given electricity demand. In addition to investment, operation and maintenance (O&M) and (where applicable) feedstock costs related to RE power plants, any assessment of the overall economic burden that is associated with their application will have to consider avoided fuel and substituted investment costs as well. Even without taking the avoided costs into account, the lower range of the RE power investments discussed above is lower than the respective investments reported for 2009. The higher values of the annual averages of the RE power sector investment approximately correspond to a five-fold increase in the current global investments in this field. [10.5, 11.2.2]

#### 7. Policy, implementation and financing

An increasing number and variety of RE policies—motivated by many factors—have driven escalated growth of RE technologies in recent years [1.4, 11.2, 11.5, 11.6]. Government policies play a crucial role in accelerating the deployment of RE technologies. Energy access and social and economic development have been the primary drivers in most developing countries whereas secure energy supply and environmental concerns have been most important in developed countries [9.3, 11.3]. The focus of policies is broadening from a concentration primarily on RE electricity to include RE heating and cooling and transportation [11.2, 11.5].

RE-specific policies for research, development, demonstration and deployment help to level the playing field for RE. Policies include regulations such as feed-in-tariffs, quotas, priority grid access, building mandates, biofuel blending requirements, and bioenergy sustainability criteria. [2.4.5.2, 2.ES, TS.2.8.1] Other policy categories are fiscal incentives such as tax policies and direct government payments such as rebates and grants; and public finance mechanisms such as loans and guarantees. Wider policies aimed at reducing GHG emissions such as carbon pricing mechanisms may also support RE.

Policies can be sector specific, can be implemented at the local, state/provincial, national and in some cases regional level, and can be complemented by bilateral, regional and international cooperation. [11.5]

*Policies have promoted an increase in RE capacity installations by helping to overcome various barriers* [1.4, 11.1, 11.4, 11.5, 11.6]. Barriers to RE deployment include:

- institutional and policy barriers related to existing industry, infrastructure and regulation of the energy system;
- market failures, including non-internalized environmental and health costs, where applicable;
- lack of general information and access to data relevant to the deployment of RE, and lack of technical and knowledge capacity; and
- barriers related to societal and personal values and affecting the perception and acceptance of RE technologies. [1.4, 9.5.1, 9.5.2.1]

*Public R&D investments in RE technologies are most effective when complemented by other policy instruments, particularly deployment policies that simultaneously enhance demand for new technologies.* Together, R&D and deployment policies create a positive feedback cycle, inducing private sector investment. Enacting deployment policies early in the development of a given technology can accelerate learning by inducing private R&D, which in turn further reduces costs and provides additional incentives for using the technology. [11.5.2]

Some policies have been shown to be effective and efficient in rapidly increasing RE deployment. However, there is no one-size-fits-all policy. Experience shows that different policies or combinations of policies can be more effective and efficient depending on factors such as the level of technological maturity, affordable capital, ease of integration into the existing system and the local and national RE resource base. [11.5]

- Several studies have concluded that some feed in tariffs have been effective and efficient at promoting RE electricity, mainly due to the combination of long-term fixed price or premium payments, network connections, and guaranteed purchase of all RE electricity generated. Quota policies can be effective and efficient if designed to reduce risk; for example, with long-term contracts. [11.5.4]
- An increasing number of governments are adopting fiscal incentives for RE heating and cooling. Obligations to use RE heat are gaining attention for their potential to encourage growth independent of public financial support. [11.5.5]
- In the transportation sector, RE fuel mandates or blending requirements are key drivers in the development of most modern biofuel industries. Other policies include direct government payments or tax reductions. Policies have influenced the development of an international biofuel trade. [11.5.6]

The flexibility to adjust as technologies, markets and other factors evolve is important. The details of design and implementation are critical in determining the effectiveness and efficiency of a policy. [11.5]. Policy frameworks that are transparent and sustained can reduce investment risks and facilitate deployment of RE and the evolution of low-cost applications. [11.5, 11.6]

**'Enabling' policies support RE development and deployment**. A favourable, or enabling, environment for RE can be created by addressing the possible interactions of a given policy with other RE policies as well as with energy and non-energy policies (e.g., those targeting agriculture, transportation, water management and urban planning); by easing the ability of RE developers to obtain finance and to successfully site a project; by removing barriers for access to networks and markets for RE installations and output; by increasing education and awareness through dedicated communication and dialogue initiatives; and by enabling technology transfer. In turn, the existence of an 'enabling' environment can increase the efficiency and effectiveness of policies to promote RE. [9.5.1.1, 11.6]
*Two separate market failures create the rationale for the additional support of innovative RE technologies that have high potential for technological development, even if an emission market (or GHG pricing policy in general) exists.* The first market failure refers to the external cost of GHG emissions. The second market failure is in the field of innovation: if firms underestimate the future benefits of investments into learning RE technologies or if they cannot appropriate these benefits, they will invest less than is optimal from a macroeconomic perspective. In addition to GHG pricing policies, RE-specific policies may be appropriate from an economic point of view if the related opportunities for technological development are to be addressed (or if other goals beyond climate mitigation are pursued). Potentially adverse consequences such as lock-in, carbon leakage and rebound effects should be taken into account in the design of a portfolio of policies. [11.1.1, 11.5.7.3]

*The literature indicates that long-term objectives for RE and flexibility to learn from experience would be critical to achieve cost-effective and high penetrations of RE.* This would require systematic development of policy frameworks that reduce risks and enable attractive returns that provide stability over a time frame relevant to the investment. An appropriate and reliable mix of policy instruments, including energy efficiency policies, is even more important where energy infrastructure is still developing and energy demand is expected to increase in the future. [11.5, 11.6, 11.7]

## 8. Advancing knowledge about renewable energy

Enhanced scientific and engineering knowledge should lead to performance improvements and cost reductions in RE technologies. Additional knowledge related to RE and its role in GHG emissions reductions remains to be gained in a number of broad areas including [for details, see Table 1.1]:

- Future cost and timing of RE deployment;
- Realizable technical potential for RE at all geographical scales;
- Technical and institutional challenges and costs of integrating diverse RE technologies into energy systems and markets;
- Comprehensive assessments of socioeconomic and environmental aspects of RE and other energy technologies;
- Opportunities for meeting the needs of developing countries with sustainable RE services; and
- Policy, institutional and financial mechanisms to enable cost-effective deployment of RE in a wide variety of contexts.

Knowledge about RE and its climate change mitigation potential continues to advance. The existing scientific knowledge is significant and can facilitate the decision-making process [1.1.8].

### U.S. Department of Energy - Energy Efficiency and Renewable Energy Alternative Fuels Data Center

# **Ethanol Feedstocks**

Almost any plant-based material can be an ethanol feedstock. All plants contain sugars, and these sugars can be fermented to make ethanol in a process called "biochemical conversion." Plant material also can be converted to ethanol using heat and chemicals in a process called "thermochemical conversion" (see <u>Ethanol Production (ethanol\_production.html</u>) to learn more about these processes).

Some plants are easier to process into ethanol than others. Some don't require many resources to grow, while others need many resources, as well as intensive care. Some plants are used for food as well as fuel, while others are cultivated exclusively for fuel production. Even residues left over from harvested crops can be made into ethanol. Climate and soil type determine the types and production potential of plants that can be grown in different geographic areas.

The U.S. Department of Energy's Bioenergy Technologies Office <u>Billion-Ton Update</u> (<u>http://www.energy.gov/eere/bioenergy/downloads/us-billion-ton-update-biomass-supply-bioenergy-and-bioproducts-industry</u>) provides extensive information about existing and potential feedstocks and availability at various price points. To view maps of feedstocks, see National Renewable Energy Laboratory's <u>Biomass Maps (http://www.nrel.gov/gis/biomass.html</u>) or use <u>BioFuels Atlas</u> (<u>http://maps.nrel.gov/biomass/</u>).



(http://maps.nrel.gov/biomass) BioFuels Atlas (http://maps.nrel.gov/biomass) Use this interactive map to compare biomass feedstocks and

Use this interactive map to compare biomass feedstocks and biofuels by location and calculate the biofuels potential for a given area.

# Starch- and Sugar-Based Ethanol Feedstocks

Nearly all ethanol produced in the world is derived from starch- and sugar-based feedstocks. The sugars in these feedstocks are easy to extract and ferment, making large-scale ethanol production affordable. Corn is the leading U.S. crop and serves as the feedstock for most domestic ethanol production. To meet requirements, the <u>Renewable Fuel Standard (RFS) (/laws/RFS)</u> limits the amount of ethanol produced from starch-based feedstocks to 15 billion gallons. This ensures there are enough feedstocks to meet demand in livestock feed, human food, and export markets.

# **Cellulosic Ethanol Feedstocks**

Cellulosic feedstocks are non-food based feedstocks that include crop residues, wood residues, dedicated energy crops, and industrial and other wastes. These feedstocks are composed of cellulose, hemicellulose, and lignin (typically extracted to provide energy for production). It's more challenging to release the sugars in these feedstocks for conversion to ethanol. Commercialization of these processes is a funding priority of the U.S. Department of Energy's <u>Bioenergy Technologies</u> <u>Office (http://www1.eere.energy.gov/biomass/)</u>.

Cellulosic feedstocks offer many advantages over starch- and sugar-based feedstocks. They are abundant and can be used to produce cellulosic biofuels required by the <u>RFS (/laws/RFS)</u>. They are either waste products or purposefully grown energy crops harvested from marginal lands not suitable for other crops. Less fossil fuel energy is required to grow, collect, and convert them to ethanol, and they are not used for human food. There are challenges with harvesting, collecting, and delivering cellulosic feedstocks. Researchers are studying these challenges to determine effective and affordable solutions to collect and deliver cellulosic feedstocks.

Potential ethanol yields from feedstocks are determined by their properties, which can be found in the <u>Biomass Feedstock Composition and Property Database</u> (<u>http://www.afdc.energy.gov/biomass/progs/search1.cgi</u>), or in the Energy Research Centre of the Netherlands' <u>Phyllis database (http://www.ecn.nl/phyllis/</u>). The table below shows the potential of some commonly considered feedstocks.

Feedstock	Theoretical Ethanol Yield (gal/dry ton of feedstock)			
Corn Grain	124.4			
Corn Stover	113.0			
Rice Straw	109.9			
Cotton Gin Trash	56.8			
Forest Thinnings	81.5			
Hardwood Sawdust	100.8			
Bagasse	111.5			
Mixed Paper	116.2			
Switchgrass*	96.7			

\*74 Switchgrass Alamo Whole Plant

Source: U.S. Department of Energy Biomass Program, Theoretical Ethanol Yield Calculator and Biomass Feedstock Composition and Property Database

The AFDC is a resource of the U.S. Department of Energy's Clean Cities (http://cleancities.energy.gov/) program.

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# Why Biofuels Can't Replace Oil

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## **Jude Clemente**

**CONTRIBUTOR** *I cover energy, environment, security, & human development.* 

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"There is growing concern about the role of biofuels in rising food prices...and doubts about the climate benefits. This has led to serious questions about their sustainability," Renewable Fuels Agency

The Energy Independence and Security Act of 2007's Renewable Fuel Standard (RFS2) orders the use of at least 36

http://www.forbes.com/sites/judeclemente/2015/06/17/why-biofuels-cant-replace-oil/#44e586b0362b

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billion gallons of transport biofuels by 2022, up from about 15 billion gallons of output today (by comparison, the U.S. now uses 140 billion gallons of gasoline and 63 billion gallons of diesel fuel each year). Of this, 16 billion gallons is expected to be from "cellulosic biofuels," which is derived from parts of plants, wood waste, and other non-food feedstocks (although only about 21 million gallons were produced in 2014). The U.S. Environmental Protection Agency (EPA) is responsible for establishing and implementing regulations to ensure compliance. Ethanol and biodiesel are the two main types of biofuels, derived from organic matter (obtained directly from plants, or indirectly from agricultural, commercial, domestic, and/or industrial wastes). To be a viable alternative for petroleum, a biofuel should provide a net energy gain, offer clear environmental and economic benefits, and not reduce food supplies and/or increase their costs. Biofuels fall short of these requirements and should therefore stay a niche market, used moderately and optionally instead of mandated at widescale public use. Environmental groups themselves have found that between 2008 and 2022, biofuels will receive more than \$400 billion in subsidies.

# **Increases Fuel and Food Prices**

A major hurdle to commercialization of biofuels is their cost in comparison to petroleum-based fuels. Lower energy density and the price of raw materials make biofuels more expensive when producing heat. And the higher the biofuel content of the fuel, the lower the energy density and thus

energy efficiency (see Fig. 1). A vital concept when considering alternatives to petroleum is the energy return on investment (EROI), or how much net energy gain resides in the finished product compared to the total energy that was used in its production. EROI measures the processes of producing, distributing, and consuming an energy source. And it directly impacts the price, rate of adoption, economic development rate, and the environmental benefits of the society that consumes it. Petroleum has an EROI of 16, versus just 5.5 for biodiesel from soybeans, which account for about 60% of U.S. biodiesel output. In reality, this means that biofuels contradict state and national goals/mandates to deploy energy efficiency as a "priority resource" to reduce both energy usage and greenhouse gas emissions. For example, released in May 2014, The White House's 40-page Energy Strategy for America mentions "efficiency" a whopping 44 times!

**Biofuels are corrosive and cause cracking in steel**, so the industry is dominated by trucks and rail, not our extensive and cheaper pipeline system. Trucks **can up** transport costs by a factor of five, and rail by a factor of three or four. This can quickly add up for Northeast states like New York and Massachusetts that want to use more biofuels: 95% of ethanol production and 60% of biodiesel production occurs in the distant Midwest. From 2007-2014, **one estimate** has U.S. motorists paying an annual \$10 billion extra in fuel costs to blend 93 billon gallons of ethanol into gasoline. Conventional heating oil that contain 2% biodiesel (now under consideration as a mandate for New York) generally cost

around 3-5 cents per gallon more, rising 1-2 cents for every percent of biodiesel contained. As a traded commodity, used cooking oil from deep fryers ("yellow grease") is regarded as the most sustainable types of biodiesel, and demand is surging. The unrefined, raw material alone is now referred to as "liquid gold," fetching over \$3 per gallon in New York City, when restaurant owners had to pay to have it taken away just a few years ago. Because of the rising value, theft and "black market" selling have followed: only 30% of waste grease in New York City is picked up by licensed collectors. Additional costs of biofuels often go unaccounted for. A study released in January by the World Resources Institute found that biofuel mandates fail to consider their opportunity costs, a common mistake made by those pushing renewables over conventional forms of energy like oil. The inconsistency of biofuels and the varying strength of blends create significant problems, particularly from a fuel efficiency standpoint. The EPA, for instance, has delayed its 2014, 2015, and 2016 RFS blending volumes due to higher prices, equipment damage (ethanol can harm engines), costly repairs, and supply shortages.

Biofuels increase food prices (plus the volatility of those prices) and therefore don't have many of the positive benefits for humanity claimed by proponents. In fact, the **UN has asked** the U.S. to suspend its biofuel mandates because it was exacerbating the food crisis: **a child dies from hunger every 10 seconds.** For the U.S. and the world, 48 million Americans live in poverty, and over 80% of the globe is undeveloped, so the rising competition between "fuel and food" is a moral issue. Consider ethanol, FarmEcon finds that with mounting ethanol production and mandates since 2006 food prices have sharply risen, and the typical American family of four has been paying \$2,055 more in food bills than would have been the case if costs had kept to the 1950-2005 trend line. Over **40%** of U.S. corn is used to produce ethanol, which has trickled down to cause **riots in Mexico City**, as one example, over higher costs for tortillas. Biodiesel demand increases the price of soybeans, and this has a tremendous trickling down effect because soybeans have literally hundreds of uses in industrial products from engine oil to crayons to food products and animal feeds. Over 98% of U.S. soy meal goes to feed pigs, chickens and cows. Today, beef, pork, poultry, eggs, and milk have had the most dramatic price increases, augmented by drought, a virus outbreak, and growing exports.

Energy markets now regularly compete with the food sector for vegetable oil, so soybean prices and energy prices have been statistically linked, creating a floor price for soy oil. Rising food and energy prices are already dangerously expanding the problem of "food insecurity." The U.S. food price index is now approaching 250, based on 100 in the mid-1980s. About **20% of those American families** with children are "food insecure." Higher domestic food prices have dire global consequences: since 2008, developing countries, already burdened with low incomes and rising debt, have constituted the bulk of U.S. food exports. Further,

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despite significant subsidies and protectionist policies, biodiesel is obviously more expensive than heating oil, still requiring government aid to survive. We know this because Platts just reported that the EPA's decision to delay the release of the RFS blending mandates has left the biodiesel market "dead." The U.S. Energy Information Administration is not projecting a significant increase in biodiesel production. As the human health (e.g., more disposable income is the basis of our health) and climate benefits (e.g., extreme weather deaths have been reduced 99% in the fossil fuel-era since 1920) of cheaper and more reliable conventional energy systems go conveniently ignored, even well intended government mandates for renewable energies like biofuels should never make us blind to market realities. The Government Accountability Office last year found that the U.S. Department of Defense had been paying up to \$150 per gallon on alternative jet fuels made from algae when oilbased jet fuels cost just \$3 per gallon.

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