Renewable resources

Manufacturing of organic chemicals has historically largely been dependent on petroleum feedstocks, a finite resource which is becoming increasingly expensive and for which renewable replacements are needed. Green Chemistry is helping to drive forward the uptake of renewable resources as a substitute for fossil feedstocks and to move towards a more circular economy approach in resource utilisation. [1]

Learning Objectives

By the end of this module you should:

- Understand the need to change the current sources of raw materials;
- Understand the different types of renewable materials available to us;

and be able to:

- Define what a platform molecule is;
- Describe the main components of biomass.

1. J. H. Clark, Green and Sustainable Chemistry: An Introduction, in *Green and Sustainable Medicinal Chemistry: Methods, Tools and Strategies for the 21st Century Pharmaceutical Industry*, The Royal Society of Chemistry, 2016, ch. 1, pp. 1-11.

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Petroleum as a chemical feedstock

The use of crude oil as a carbon feedstock for the manufacture of chemicals has dominated the industry with few exceptions, for example a small percentage of naturally-derived compounds (e.g. for use in personal care products and pharmaceuticals). [1] In this video Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York outlines where our dependence on crude oil derives from.

1. J. H. Clark, Green and Sustainable Chemistry: An Introduction, in *Green and Sustainable Medicinal Chemistry: Methods, Tools and Strategies for the 21st Century Pharmaceutical Industry*, The Royal Society of Chemistry, 2016, ch. 1, pp. 1-11.

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Bulk molecules from crude oil

In this video Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York explores how crude oil is processed to the chemical commodities we use today from enormous quantities of a small number of simple molecules (base chemicals). He also discusses the volumes of these base chemicals that are required annually which demonstrates the full nature of the challenge of replacing petroleum derived feedstocks with renewably derived feedstocks.

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And when we take a closer look at how we actually go from fossil resources through to

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products, there's something really quite important to note about how our industry functions.

And that's that from this feedstock, the first thing we actually do for our chemical industry is rely very heavily on just large quantities, but only a small number, of very simple molecules that have some kind of functionalities, so predominantly they are either aromatics or alkenes, with the exception of methanol, but these are the building blocks for the vast majority of our chemical industry.

And we refer to these as our 'Base Chemicals' and then from these we then go on to make commodity chemicals and then from these we'll go on to make an array of products and this is really, you know, obviously an overly simplified version, but hopefully what you can see is we go from just a few simple building blocks up too many, many products.

And what we're having to do progressively as we go along here is really add functionality into the whole system.

So we start with a little bit of functionality on some simple molecules and as we progress across to our products with we're putting functionality in.

And as I mentioned earlier, what's really key about these base chemicals to support our industry is that they are available on an enormous scale.

So if you're looking at the data from 2010 for the production of these base chemicals, you can see that their quantity produced in that year is really quite astronomical, especially so for ethene and for propene and for the aromatics like xylene.

And if we look at that the data for that year and see how much crude oil is extracted, so we've got around 360 million tonnes in total of these base chemicals produced and in that same year we took about 3.6 billion tonnes of crude oil out of the ground.

So roughly about ten percent of that crude oil is going off to make chemicals, the rest is used for fuel, energy and a little bit is used for things like asphalt or materials like that.

Some of these basic chemicals have already been looked at and are being produced from biomass as we speak.

But if you look at the quantities it's really only just touching the very edge of the quantities we need, so actually a lot of people get excited about Braskem and the quantities of bio-based ethene that they're producing in Brazil from sugar cane, but

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again its quantity really is only tiny.

Still, it does show that the technology is there.

So what we're doing here is we're dropping in replacements.

So we've got a chemical structure for these base chemicals and what we're looking at here is to make the exact same chemical structure, but from biomass.

But some of them will always pose major challenges so benzene, toluene and xylene actually look really quite challenging to generate from biomass.

And when we take a closer look at pharmaceuticals later, we'll see actually there is a difficulty for us regarding aromatic compounds..

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Biomass as a chemical feedstock

This material taken from J. H. Clark, Green and Sustainable Chemistry: An Introduction, in *Green and Sustainable Medicinal Chemistry: Methods, Tools and Strategies for the 21st Century Pharmaceutical Industry*, The Royal Society of Chemistry, 2016, ch. 1, pp. 1-11. .

Large volume, low value bio-resources, collectively described as biomass, that are able to be replenished on a reasonably short time-scale, can be used as a feedstock for making chemicals, materials and fuels. Biomass includes:

- Forestry residues;
- Short rotation trees;
- Agricultural residues including straws;
- Food processing wastes including shells, stones, peels;
- Grasses and other land grown biomass;
- Marine residues;
- Macroalgae (seaweed) and microalgae;
- Other food wastes.

The use of waste biomass is advantageous as it avoids competition for agricultural land which might be used for food production, while simultaneously adding value to waste streams that would potentially otherwise go to landfill. As well as functional molecules that can be extracted from biomass, it is also possible to biochemically and/or thermochemically process the bulk components of biomass to give a range of additional useful functional molecules or 'platform molecules', such as succinic acid, lactic acid and levoglucosenone.

The biorefinery and platform molecules

In this video Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York sets out how biomass can be used to construct an analogous process to the current

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oil-refinery based chemical industry via a ‘biorefinery’ concept. He focusses on the development of a new set of molecules derived from biomass, ‘platform molecules’, that can be used as building blocks for a bio-refinery based chemical industry and the associated processing technologies employed in their production.

Platform molecules were defined in a report produced by people working for the US Department of Energy. In this report 12 building block chemicals were identified, which can be made from sugars either by fermentation or synthetically. These chemicals can subsequently be converted to a number of high-value bio-based chemicals or materials.

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Components of biomass and their conversion

In this video, Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York outlines the major constituents within biomass available for refining, and how the composition of the biomass dictates the most suitable platform molecules to produce.

Although initially a biorefinery may focus on a single target molecule or group of molecules e.g. a high value, low volume extract, to maximise the efficiency of crude biomass processing a useful strategy is to valorise as many of the constituents within the biomass as possible. For example, after first removing high-value, low-volume extracts (terpenes, triglycerides, waxes, sterols, pigments, aromas etc.), the next step would be to target easily accessed or processed components (sugars, starches and hemicellulose), before recovering the protein (potentially for feed) and finally processing the recalcitrant lignocellulose.

In the following sections, four of the main constituents of biomass (saccharides, lignin, protein and extracts) will be examined in turn to look more closely at the types of molecules that can be made from them and their inherent functionalities.

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So I mentioned already the importance of noticing the difference in the feedstocks when we compare the two chemical industries so for possible resources.

Simply put, crude oil is relatively simple for us as chemists to look at, it's composition isn't overly complex and it's almost devoid of heteroatoms.

Whereas biomass contains oxygen, sulphur, nitrogen and all of this means that we lead to a far more complex feedstock and this has important implications for the sorts of platform molecules that we can produce.

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So biomasses composition is more complicated than crude oil and hopefully you're already aware of what are the major constituents within biomass.

So polysaccharides really dominate; some of these could be in competition with food, so something like starch, then you've also got structural polysaccharides such as cellulose, hemicellulose and maybe even things like chitin from crab shells.

There are also then, our sugars, our mono- and disaccharides and these very much have competition with food so this is interesting when we consider the example of Braskem and its production of ethene from biomass where they currently would grow sugarcane and then extract the sugar, from there convert it to ethanol and dehydrate to ethane, but obviously this does cause issues with competition with food.

It's worth bearing in mind this competition with food as well isn't just simply whether the biomass we produce is something we want to eat but it's also whether we're growing it on land which we might normally use for growing food.

And then we have lignin which is the major aromatic portion of biomass and it can form quite a large percentage of biomass but it's actually really quite hard for us to process and to get the aromatics out.

Then we've got things like protein and then finally we come down to stuff like our extract so this essentially is all the other stuff that's in there in biomass.

It might be things normally in very low quantities, often in quite complex mixtures, but it's these which can often carry quite a lot of high value as well.

And then we know that these are the constituents of biomass, but actually when we're looking at using biomass it's probably going to be much more complicated because these are all mixed together and then also different plants, plant material may be mixed together and it just further complicates things for us.

When we think about trying to categorize and simplify our big list of platform molecules one of the ways that this is typically done is to actually characterise by the feedstock that we're using and this is because different feedstocks, different constituents within that biomass will allow us to produce different platform molecules.

So it's really important we understand well the makeup of our bio mass because it's that will dictate the sorts of molecules that we can generate from it.

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And as such, probably as a biorefinery operates it will do its best to try to separate the constituent parts of biomass prior to producing platform molecules so it has better control and better selectivity of the platform molecules it produces.

so there is a good chance, and certainly a lot of processes out there now actually sort of use lignin and cellulose and possibly hemicellulose and sort of treat it all as one entity and actually the lignin typically ends up just being left as a waste product.

So also it's worth bearing in mind with biomass that actually we now have this issue where seasonality and species variation could be something important for us to consider in the future.

This isn't the case when we're looking at crude oil; it's already been in the ground for millions of years and so from summer to winter doesn't really change.

From location to location globally there is some difference but it's not enormous, it is not the same difference that we would have when we think about our biomass feedstock.

So I think this is a great challenge for biorefineries but already work is on-going to try to see how you can have a biorefinery operating more effectively throughout the entire of the year..

Saccharides

In this video the refining options for the saccharide fraction of biomass are discussed by Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York.

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We'll start with saccharides.

This is our sugars and also our polysaccharides.

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As you can see at the top here, this really is the major constituent of biomass, and really probably is our greatest hope in generating platform molecules on a large scale, in a large quantity, every year.

To begin with, we've got fermentation processes.

So we could just extract sugar or probably what holds a greater hope for the future is taking this cellulose, breaking this down to sugar and then fermenting that sugar through to product.

Ethanol is well-known, this is what Braskem's route is to its bioderived ethene.

Itaconic acid, this is an interesting molecule because since the 1960s, this diacid has been produced from fermentation industrially, as opposed to a chemical route so if you buy itaconic acid now, it will actually be bio-based.

Then you've got something like some of the amino acids which includes glutamic acid.

This is important because we'll look later at proteins; actually a more selective route to a specific amino acid will probably be from a fermentation route.

The furans: so this is where we start to strip functionality out of our sugars.

These are normally begun through thermal or chemical processes.

HMF is a very interesting furan which will eventually be used as a replacement for PET, for plastic bottles.

We're going to look at CMF later.

Reduced sugars; so this is simply hydrogenation of sugars but these polyols find a lot of applications.

And then we've got anhydrosugars; again much like the furans and often they appear together, this is where we're taking some of the functionality out of our sugars through dehydration so you've got levoglucosan and levoglucosanone..

Lignin

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In this video the refining options for the lignin fraction of biomass are discussed by Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York.

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Protein

In this video the refining options for the protein fraction of biomass are discussed by Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York.

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Extracts

In this video the refining options for the extracts within biomass are discussed by Dr Tom Farmer at the Green Chemistry Centre of Excellence, University of York.

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Multiple choice questions

1. What are the key technical differences in terms of processing between base chemicals from petroleum and bio-based platform molecules for the chemical industry?
   1. Bio-based molecules will have a larger amount of radioactive ^{14}C
   2. Petroleum-based molecules are more abundant than bio-based ones
   3. They cannot make the same molecules
   4. They contain different major functional groups; hydrocarbon (olefins and aromatics) vs heteroatoms (alcohols, amines, carbonyls and acids)
   5. Crude oil is hazardous to handle, whereas biomass is safe
   6. A molecule made from petroleum will have different properties to one made from biomass.
2. Which are the main groups of biomass employed for producing platform molecules?
   1. Fatty acids
   2. Proteins
   3. Minerals
   4. Saccharides
   5. Lignin
   6. Extracts
   7. Vitamins
3. What factors contribute to variability in biomass feedstock?
   1. Land management
   2. Seasons
   3. Geographical location
   4. Processing methods
   5. Species type
   6. Weather

Answers on last page

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Summary and further reading

The advantages of using biomass as a chemical feedstock are manifold and a wide range of bio-derived chemicals are already available on the market. However it is essential that green methodologies are applied to the production of these bio-derived chemicals to ensure that they are genuinely sustainable. It is also critical that they are assessed within a lifecycle context to include the wider implications e.g. in terms of land use and competition with food.

Recommended reading:

J. H. Clark and F. Deswarte, *Introduction to Chemicals from Biomass*, John Wiley & Sons Ltd, Chichester, UK, 2ndnd edn., 2015.

J. H. Clark, Green and Sustainable Chemistry: An Introduction, in *Green and Sustainable Medicinal Chemistry: Methods, Tools and Strategies for the 21st Century Pharmaceutical Industry*, The Royal Society of Chemistry, 2016, ch. 1, pp. 1-11.

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