

## **The Chemical Industry, Past Present & Future** by **Dr Ron Bennett** on 15 January 2021

Dr Bennett began by showing a graph of projected World Primary Energy Sources. Reading up from the bottom: Oil peaks about now, but Natural Gas and Coal peak around 1930, these all remaining significant thereafter. Nuclear and Hydro slowly rise from a low base throughout. Wind and Solar grow continuously.

However, CO<sub>2</sub> emissions into the atmosphere should reduce from current levels from these sources.

Not all oil, gas & coal is burnt, a growing proportion is used as a chemical feedstock (ca. 14% currently from oil) with plastic the major product.

Dr Bennett set the scene with billion tonnages/year of:

- Crude Oil 4.5
- Natural Gas 3.5
- Shale gas 0.4
- Coal 5.5
- Steel 1.9
- Cement 4.1

Oil, gas & coal extraction; and particularly steel (8%) & cement manufacture (8%) are all major global CO<sub>2</sub> emitters.

Dr Bennett showed another projected graph of worldwide Chemical sales, with China supplying 50% of them by 2050 in a market almost twice 2017 (pre-covid) levels. Others may see growth, but not in proportion.

He followed it with the Top 10 Industrial Chemicals (quantities in megatons per annum): Sulfuric Acid (270); Ammonia (235); Ethylene, C<sub>2</sub>H<sub>4</sub> (190); Oxygen; Methanol (148); Propylene, C<sub>3</sub>H<sub>6</sub> (120); followed by: Chlorine; Ethylene Dichloride, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>; Phosphoric Acid; Caustic Soda.

**Sulphuric acid** was the bedrock of the Industrial Revolution; 75% is now consumed in making superphosphate, and other fertilizers. Production increased from around 1760 when it became a starting material for synthetic bleaching agents for fabrics in place of traditional techniques using soured milk. It was said that the consumption of sulphuric acid in any country together with that of iron, reflected its industrial strength. The manufacture of bronze, iron and ceramics are centuries old, are all chemical processes but these Inorganic processes will not be discussed further as the scope of the talk will be restricted mainly to those chemicals we now produce from coal, oil or gas.

In the beginning everything came from Nature, and all Organic Chemicals were derived directly from natural products. The first significant organic chemical processes were those based on products from wood. When heated at up to 400°C, **Wood** can give charcoal (35%) and; if emitted vapours are condensed, wood gas (15%), light oil and crude vinegar (5%) – which can be distilled and refined – or wood tar (20%) from which creosote is derived.

**Coal** when destructively distilled at 800°C provides coke and volatile components – passing these through water dissolves soluble gases and condenses volatile chemicals leaving coal gas. The aqueous layer on standing separates to give ammoniacal liquor over a layer of coal tar. Coal tar can then be distilled to separate fractions: light oil (Benzene, Toluene, Zylene); middle oil; and heavy oil (Creosol, Naphthalene, Naphthol); and Anthracene oil.

Chemicals derived from Coal-based feedstocks in the early years: Perkin led the way in 1856 by producing Aniline dye. Many more dyes followed. In 1884 Gram found that bacteria in a smear could be seen if stained with crystal violet. Gram +ve bacteria would keep the violet colour; Gram -ve bacteria would not but could be stained red with safranin. This distinguishing feature remains a useful test. Synthetic drugs were developed including Aspirin (Hoffman 1899); and Salvarsan (Ehrlich 1907), an organo-arsenic compound which was the first modern antimicrobial agent and the first effective treatment for syphilis and African trypanosomiasis.

Bakelite (Baekeland 1909) a phenol/formaldehyde resin, and the world's first synthetic plastic, was another coal-based product.

These chemical developments, based around the products of dry distillation products of coal which are mainly Aromatic molecules, contrasts with products derived from oil which are mainly Aliphatic.

Calcium carbide, first manufactured in 1892, in an electric arc furnace from a mixture of lime and coke at approximately 2,200°C is mainly used to make acetylene.

Ammonia, made by the Haber Bosch Process, reacted hydrogen from methane and atmospheric nitrogen over an iron catalyst at 200 atmospheres at 400°C - it was commercialised in 1913.

Ammonia is the raw material for nitric acid and nitrate production and was essential for Germany in WW1 as a replacement for imported nitrates used in explosive production.

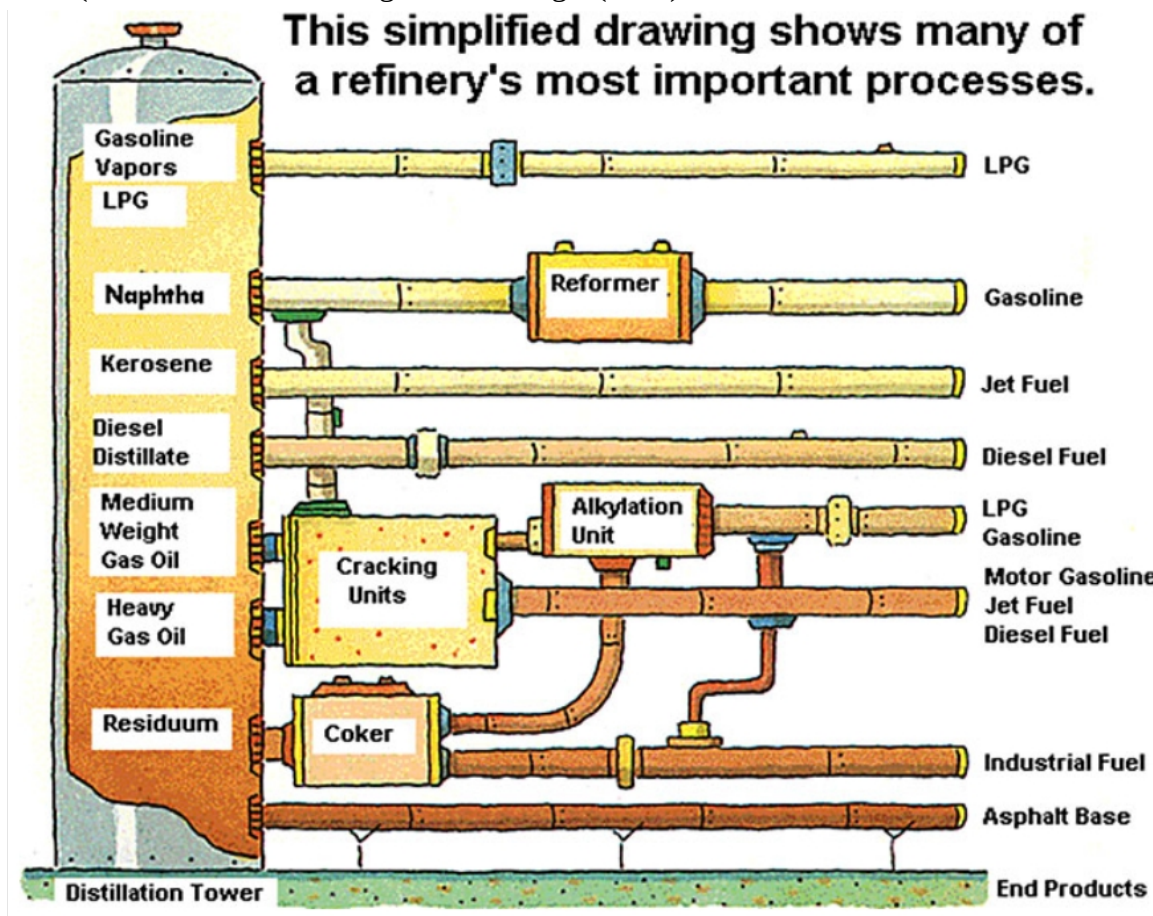
**Crude Oil** may be Light, Medium or Heavy, comprising compounds with differing numbers of carbon atoms, from 1 (C<sub>1</sub>) to over 50 (C<sub>50</sub>), ie from gasses to bitumen. It may be Sweet (< 0.7% Sulphur) or Sour.

Light Sweet is most sought after (and expensive), with most light fractions and least tars. Medium is more common and meets most demand. Refineries Distil, Crack, and Reform Oil to optimise the product mix.

*Distillation:* a crude oil may have a viscosity corresponding to C<sub>40</sub> compounds, and contain, in high-to-low order of both of viscosity and boiling-point: Bitumen (>C<sub>50</sub>), Paraffin Wax (C<sub>40</sub>-C<sub>50</sub>), Fuel Oil (C<sub>30</sub>-C<sub>40</sub>), Lubricating Oil (C<sub>20</sub>-C<sub>30</sub>), Diesel (C<sub>16</sub>-C<sub>20</sub>), Paraffin (C<sub>10</sub>-C<sub>16</sub>), Naphtha (C<sub>6</sub>-C<sub>50</sub>), Petroleum (C<sub>5</sub>-C<sub>6</sub>), & Gas (C<sub>1</sub>-C<sub>4</sub>). These can be separated out by distillation.

*Cracking:* breaking up large hydrocarbon molecules to make smaller molecules which increases the yield of gasoline fuel and to provide the building blocks for the chemical industry. It can be Thermal – heating the hydrocarbons in a still: under pressure; Catalytic, at a lower temperature (around 350°C) and pressure with a catalyst; or briefly with Steam at 900°C at high pressure, this producing low unsaturated hydrocarbons.

*Reforming:* changing the shape but not size of hydrocarbon molecules to make aromatics in particular (their structure including benzene rings, (C<sub>6</sub>H<sub>6</sub>)). This raises the octane number of fuels.



**Fischer–Tropsch process** is a series of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. These reactions occur in the presence of metal catalysts, typically at temperatures of 150–300°C and pressures of one to several tens of atmospheres. The process was first developed by Franz Fischer and Hans Tropsch at the Kaiser-Wilhelm-Institut für Kohlenforschung in Mülheim an der Ruhr, Germany, in 1925.

### Some Basic Hydrogen Reactions

Most need energy input (-ve kJ/mol), some release energy (+ve kJ/mol)

Sebatier 1897	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-165 kJ/mol, 300-400°C, 30bar, Ni catalyst
Steam-Methane Reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	-206 kJ/mol
Water –Gas Shift Reaction	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2$	+ 41 kJ/mol
Bergius Process (1913)	$n\text{C} + (n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2}$	Carbon = coal, 400-500°C 200-700 bar
Fischer-Tropsch Process	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	-165 kJ/mol Carbon = red hot coke
	$n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$	-180 kJ/mol, 220-270°C, 200-250 bar, Co cat

**Electrochemical Reactions** - while preparative electrolysis of organic molecules has been an active area of research for the past century, modern synthetic chemists have generally been reluctant to adopt this technology. The only large scale organic electrochemical process in current use is for manufacture of Adiponitrile, a precursor for Nylon 6,6

In fact, electrochemical methods possess many benefits over traditional reagent-based transformations, such as high functional group tolerance, milder conditions, and innate scalability and sustainability.

For electrochemical processes to be adopted there must be sufficient economic Electrical Power and a real desire to reduce pollution and CO<sub>2</sub> levels.

Higher efficiency Electrochemical Cells can be achieved by improving electrode technology and developing new hydrophobic and hydrophilic functional groups (for better contact between reagents and the active catalytic surface).

### A Carbon Neutral Hydrogen Manufacturing Policy

- We can produce Hydrogen (and Oxygen) by electrolysis of water commercialised
- CO<sub>2</sub> can be reduced to CO electrochemically (each kg needing 9 kWh of power) commercialised
- We can then Either combine CO with Hydrogen by a Fischer Tropsch process commercialised
- OR combine Carbon Dioxide with Water directly to form Building Block Molecules in development

Various products can follow from the CO<sub>2</sub> +H<sub>2</sub>O reduction reaction - here they are priced:

- Carbon Monoxide, CO	0.6 \$/kg	- Methane, CH <sub>4</sub>	0.18 \$/kg
- Formic Acid, HCOOH	0.74 \$/kg	- Alcohol, C <sub>2</sub> H <sub>5</sub> OH	1 \$/kg
- Methyl Alcohol, CH <sub>3</sub> OH	0.58 \$/kg	- Ethane, C <sub>2</sub> H <sub>6</sub>	1.3 \$/kg

### Biodegradability of Plastics

There is considerable confusion about aspects of plastic recycling, biodegradability and compostability

- Many plastics such as Polyolefins and Polyester, used extensively in packaging, do not degrade easily
- Alternatives offered as biodegradable or compostable alternatives do not degrade in nature readily and therefore will not solve the problems of river and ocean pollution

As an example Dr Bennett compared PHA with PLA, two polyesters made from natural renewable products– indeed PHAs are made naturally in an organism in high yield and only have to be physically extracted (i.e. no external chemical process necessary) PHA (Poly Hydroxy Alkanoate) are a family of biodegradable plastics with PHB being the most common and commercialised (but expensive). PLA (Poly Lactic Acid) is made from lactic acid monomer, itself made by a fermentation process.

In a standardised Simulated Ocean test PHA4100 ( a PHB) degraded by 80% in a year and PHA2200 to 50%, as did a Cellulose bag. However, a PLA bag was little better than a Polythene bag, at less than 10%.

**Future** – Dr Bennett outlined what he saw as the way the Chemical industry will develop, not only in areas he had discussed but in biochemistry. He reiterated aspects he had mentioned earlier about environmental problems, particularly in mining – China has ‘cancer villages’ where they mine rare-earth minerals, and the humanitarian and pollution problems at the Cobalt mines in the Congo.

- Fossil Fuels remain important for next 30 years - Coal and Fracking still growing.
- Methane to chemicals grows with new technology (‘methane to methanol’ at 70% efficiency);
- Oil Companies increasing Chemical manufacture as Fossil derived fuels shrink;
- Electricity becomes dominant energy source and Electrochemistry uses basic molecules CO<sub>2</sub>, N<sub>2</sub> and Water as feedstocks;
- Plastics not declining in Volume; but packaging plastics change to PHA;
- Partial use of hydrogen to replace coke in Steel mills (75% of Steel made from Iron Ore);
- Ores for batteries and high-Tech applications causing environmental problems as recycling the extracted materials is prohibitively expensive, unlike organics such as C, H or O;
- Chemistries of the future aim to be environmentally friendly and focus on Materials Science and Biotechnology.

He closed with a slide showing a cell whose anode and cathode are separated by a bipolar membrane. Researchers in Switzerland have developed a catalyst, made entirely from earth abundant materials, that allows solar-generated electricity to reduce the environmental pollutant carbon dioxide to carbon monoxide, a valuable chemical feedstock. In the cell CO<sub>2</sub> is pumped into the cathode side, where CO is generated, the displaced oxygen is released at the anode.