

Clean Burn

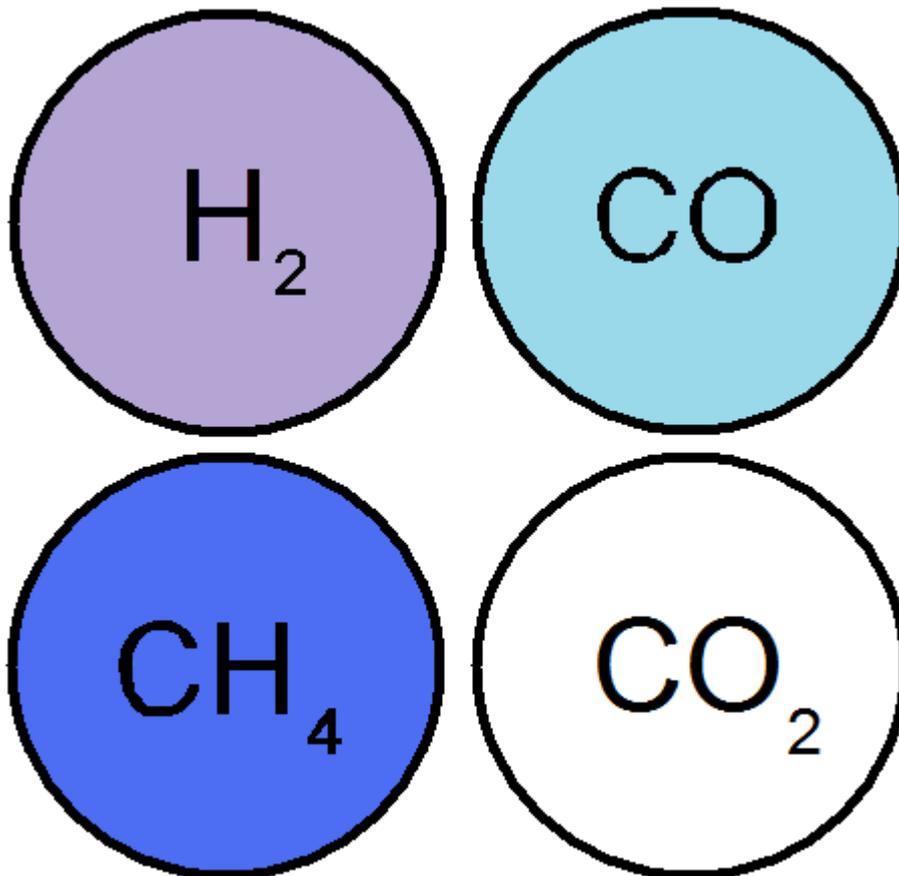
The Transition to Renewable Gas

by Jo Abbess

SUPPLEMENTARY MATERIAL TECHNICAL ESSAY

Version 1

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The Chemistry of Gas

Introduction

Natural Gas will remain a popular energy fuel for several decades to come, but although it burns cleaner than coal, it will eventually overshoot carbon dioxide emissions budgets imposed by climate change control policy. The alternative to high carbon fossil gas from below the ground is low carbon manufactured gas, produced on the surface of the Earth. This Renewable Gas can be introduced gradually, supplementing and then replacing Natural Gas in energy systems.

The fossil fuel sector is likely to be one of the main architects of Renewable Gas systems, because of an increasing demand for hydrogen in petrorefinery. This hydrogen needs to be supplied without causing rising carbon dioxide emissions from refinery, which implies change in processing plant; and this will probably lead to the development of Renewable Hydrogen production.

Because the oil and gas production and refinery industry is potentially key in the transition to low carbon gas, it is therefore useful to have some comprehension of what the petroleum industry is occupied with. And in order to do that, it is necessary to cover some geology and chemical process engineering in outline.

1 The chemistry of Natural Gas

1.1 The origins of gas and oil

1.1.1 Source rock

What is known as "source rock" is formed by the sedimentation of material with significant amounts of organic compounds, originating from plants and animals, deposited under anaerobic or anoxic conditions, over geological time (see Table 1). Sedimentary basins form in a variety of ways (MIT, 2007, Lecture 15), including in shallow seas, at the bottom of lakes, and at river deltas (Einsele, 2000). In the initial phase of shallow burial, the organic material may become oxidised, or decomposed by micro-organisms, which may by-produce methane gas ("biogenic" Natural Gas, see Table 10). During the course of time, the organic sediments will become covered with later deposits (overburden) or may be folded under other strata through crustal deformation. If the organic material is prevented from total decomposition or oxidation at the time it is first deposited, for example by the enduring presence of water, say, from abrupt sea level rise due to climate change, accumulating ice sheets, or coastal or marine shelf collapse, it can then be carried far down into the Earth's crust through tectonic subduction. There, it will be subject to heating from the Earth's core, sufficient that it may end up eventually producing petroleum oil and "thermogenic" Natural Gas (see Table 10), which is mostly methane (Tissot and Welte, 1984, Chapter 7). In many locations where oil and gas are found, it can be seen that much of the organic material that was originally present in the "immature" source rock must have thermally decomposed and migrated away to another stratigraphic formation. By contrast, source rock that has not yet matured can have high levels of organic matter. Oil shales, for example, can typically have 2% - 50% of Types I and II of the organic material kerogen (Schobert, 2013, Pages 116, 189), or more

(Yen and Chilingarian, 1976)), and sapropelic ("waxy") coals (Tissot and Welte, 1984, Chapter 8) have more than 50% Types I and II kerogen (Schobert, 2013, Page 116). Humic ("woody") coals, for example, the Euramerican, have a very high proportion of Type III kerogen (Pashin, 2008). Coals are defined as sedimentary material with more than 80% organic matter (Padley, 1995). Much of the world's production of oil and gas to date is thought to have originated in source rock with somewhere between 2.5% and 10% total organic carbon (Verweij, 1993, Section 3.1.4). The amount of organic material that was sedimented was possibly dependent on the rate of climate change (Vandenbroucke and Largeau, 2007, Section 4.2.1).

Table 1 Geological Elements of a Classical Petroleum System

Source Rock	Sedimentary strata which, when they were laid down, were rich in organic matter
Migration Pathway	Source rock produces hydrocarbon oil and gas which can migrate under pressure (expulsion)
Reservoir (Reservoir Rock)	Porous or fractured strata in which a pool of hydrocarbon oil and/or gas can reside after migration
Tight Gas	Gas that does not migrate from its Source Rock
Tight Oil	Oil that does not migrate from its Source Rock
Seep	Hydrocarbons that migrate out of the Earth's crust to ocean, land surface or air
Trap	A geological formation that allows hydrocarbon oil and gas to accumulate
Seal (Cap Rock)	A geological formation that prevents hydrocarbon oil and gas from dissipating
Pool	An accumulation of hydrocarbon gas or oil in Reservoir Rock
Salt	Sedimentary strata relatively high in salts, the result of evaporation. Can form a Seal.
Shale and Mudstone	Sedimentary layers built from silts, muds or clays. A shale or mudstone bed can form a Seal.
Graben	A rift or trough ("grave"). Can form a Trap.
Sand	Sedimentary strata formed from sands. Can form a Trap.

1.1.2 Kerogen

Kerogen is composed of relatively high molecular weight compounds of organic origin, insoluble in organic solvents, and is contained in sedimentary source rock (Durand, 1980). It is formed by the geological process known as diagenesis, the physical and chemical alterations of sedimentary materials, as a result of common geological processes, under the action of somewhat increased temperatures and pressures, in a place of "shallow burial" (MIT, 2007, Lecture 9). Organic material under these conditions undergoes differential chemical alterations : some lipids (oily and fatty substances) will be chemically preserved and become a constituent of bitumen, and are known as "biomarkers" (Killops and Killops, 2005, Page 135); whilst carbohydrates, amino acids, proteins, lignin and other components will be chemically modified to form constituents of kerogen, either directly, or after first being transformed into humic substances (Killops and Killops 2005, Figure 4.11). If the kerogen continues to be driven deeper into the Earth's crust, where it is warmer, it can undergo a second stage, catagenesis (sometimes "katagenesis"), during which it can expel hydrocarbons, such as crude petroleum oil and some methane gas. These can migrate away from the source rock to oil and gas reservoirs (England et al., 1987). The deeper the remaining kerogen travels, the more likely it will start to produce a mixture of liquid and gaseous hydrocarbons ("wet gas" or "condensate"). If the kerogen goes deeper still, it can undergo metagenesis, where it may still be able to produce methane gas ("dry gas") until its hydrogen content becomes very low (Allen and Allen, 2013, Figure 11.24). The highest temperature for hydrocarbon generation is about 230

degrees C (Killops and Killops, 2005, Chapter 4, Page 148). As kerogen of all kinds is translated deeper into the Earth's crust, there is an "oil window" - for humic coals as well as sapropelic kerogens, although it is far smaller (Killops and Killops, 2005, Figure 4.20). Methane gas is generated from kerogen at almost all depths (Allen and Allen, 2013, Figure 11.23), and when kerogen generates oil, the oil can subsequently be thermally "cracked" to gas (Allen and Allen, 2013, Figure 11.21). Carbon dioxide gas generated from the kerogen itself may reduce with depth (Pashin, 2008, Figure 9.3), but carbon dioxide originating from surrounding rocks may get trapped in the reservoir and form part of the oil or gas in place (Fleet et al., 1998; Wycherley et al., 1999). Hydrogen sulfide generation increases with depth (Pashin, 2008, Figure 9.3).

1.1.3 Bitumen

Bitumen is composed of viscous high molecular weight compounds (asphaltenes) and lower molecular weight (maltenes) of organic origin (Shell, 2003), soluble in organic solvents, and is contained in a variety of sedimentary source rock formations. Bitumen may be formed during diagenesis, at the expense of kerogen formation, or bitumen may be formed from kerogen or its successor chemicals during later stages of thermal change (Azri, 2013; Tissot and Welte, 1984, Chapter 4). As such, it is a residue from the processes that generate crude oil and Natural Gas. As with other residual petroleum accumulations - heavy oil, extra-heavy oil and oil sands, it is thought that bitumen can generate further oil and gas if its original catagenesis was incomplete, and it is then subjected to thermal degradation from downwards relocation in the Earth's crust (Zhang et al., 2007). Extreme thermal degradation of bitumen leads to insoluble pyrobitumen forming as a final residue of hydrocarbon generation. The presence of pyrobitumen could influence the ability of kerogen to produce oil, which suggests that more complex hydrocarbon reservoirs, where there has been differential ageing, may not be good prospects for liquids production (Pan et al., 2012).

1.1.4 Stages of kerogen decomposition

Kerogen can be reactive or inert. If it is reactive, it may produce oil and gas through thermogeological decomposition; if inert, it will not (Allen and Allen, 2013, Figure 11.21). Reactive kerogen may be labile or refractory (Quigley and Mackenzie, 1988). Oil-bearing kerogen is mostly of the labile kind, which activates at around 100 to 150 degrees C (Celsius) to form crude petroleum oil or simply "crude oil" (Quigley and Mackenzie, 1988); the "Golden Zone" in the Earth's crust for petroleum accumulation being where temperatures are between approximately 60 and 120 degrees Celsius (Allen and Allen, 2013, Figure 11.57), and the High Pressure High Temperature (HPHT) reservoirs being between 120 and 150 degrees Celsius (Nadeau, 2011). Gas-prone kerogen is mostly of the refractory kind, and it breaks down at higher temperatures - around 150 to 200 degrees C in the "gas window" (Quigley and Mackenzie, 1988). Petroleum oil, once formed, may decompose to give gas if the temperatures are in the region of 150 to 190 degrees C (Allen and Allen, 2013, Figure 11.21).

There are many different formations of rock that are categorised as containing organic material liable to experience petroleum formation processes. The three main groups currently recognised are : liptinite (formerly known as exinite), huminite/vitrinite and inertinite (Suarez-Ruiz, 2012). The sub-divisions enable more accuracy, and include : alginite, textinite, fusinite, resinite and fluorinite (e. g. Sykorova et al. 2005).

1.1.5 Grades of kerogen

There are four types of kerogen recognised. For oil and gas exploitation the most important types are I, II, II-S (Type II and high in sulfur-bearing constituents) and III (Lewan and Henry, 2001) :-

Type I : Mostly formed from micro-organisms, mostly from algae and bacteria (Padley, 1995, Section 2.1.5), mostly deposited as sediment in undisturbed aquatic environments such as lake beds (lacustrine) or lagoons (Vandenbroucke and Largeau, 2007, Section 4). Type I kerogen is mostly labile (Verweij, 1993, Section 3.1.5), and has the highest potential to produce petroleum oil on maturation under deep geological conditions (Killops and Killops, 2005, 4.4.3, (a)). However, Type I kerogens are calculated as producing less than 3% of the world's oil and gas (Vandenbroucke and Largeau, 2007, Section 4.3.2).

Type II : Mostly formed in relatively shallow marine settings, mostly from phytoplankton (algae), zooplankton, and bacteria (Padley, 1995, Section 2.1.5), together with plant material (Killops and Killops, 2005, Section 4.4.3, (b)); the plant material potentially originating from a terrestrial setting (Spiker et al., 1988). Type II kerogen has more labile material than refractory (Verweij, 1993, Section 3.1.5), and has a lower yield of hydrocarbons than Type I, but is the source of gas and oil in many provinces. The main difference between Type II and Type I kerogen is that Type II kerogen has a significant proportion of heteroatoms (sulfur, oxygen or nitrogen) (Killops and Killops, 2005, 4.4.3, (a)). Normal levels of sulfur are up to 6% (Padley, 1995, Section 2.1.5), but there is a high sulfur sub-category known as Type II-S or Type IIS, "Sulfurous" (Stankiewicz et al., 1996), with somewhere between 8% to 14% sulfur (Padley, 1995, Section 2.1.5). The oil window for Type II-S kerogen may begin at lower temperatures, depending on associated strata (Bordenave, 1993, Section 4.3)

Type III : Mostly terrestrial plant matter, such as from trees, dispersed in an mineral matrix (Killops and Killops, 2005, Section 4.4.3 (c)). When this type of organic material is deposited in a swamp environment, in the early stages it is known as peat (Schobert, 2013, Section 8.4), and its diagenesis and catagenesis are known as coalification, and under conditions of severe compaction can finally produce coals. Type III kerogen from source rocks or coals is much less likely to produce oil than Types I and II, and more likely to produce gas, if sufficiently mature (at the correct depth and age). Most coals are composed largely of Type III kerogen ("humic coals"), but some are composed largely of kerogen that more resembles Type II - "sapropelic coals" (Liu et al., 2003) - and these are considered to have originated as organic muds or oozes of non-woody material in freshwater environments (O'Keefe et al., 2013, Section 1.2.2).

Type IV : This is considered inert. Sometimes it is not considered a true kerogen, as it has no hydrocarbon production potential. At very high temperatures and pressures underground it may form graphite.

Oil and gas-bearing kerogen can be simply divided into two categories : sapropelic (Types I and II) and humic (Type III), and these correspond to the original organic content deriving mostly from "algal" (Types I and II) or "woody" (Type III) sources (Spiker et al., 1988, Figure 1).

1.1.6 Types of oil and gas wells

Oil and gas wells can be of several kinds that correspond to the stage of kerogen decomposition (see Table 2). Crude oil wells are drilled for liquid hydrocarbons resulting mainly from the early stages of kerogen catagenesis. The Natural Gas in these wells is known as "associated gas", and in the original reservoir state it can be dissolved in the oil ("dissolved gas", or "solution gas"), or be separate, in a pocket outside the oil ("free gas"). Drilling an oil well can change the pressure in the reservoir, and dissolved gas can then vapourise to form a "gas cap". This "oil well gas" is "rich" or "wet", as it will inevitably contain a good fraction of hydrocarbons with a heavier molecular weight than methane, owing to its co-presence and co-formation with oil. The gas found associated with crude oil causes the wells to have a high reservoir pressure, and enables the oil to be produced at the wellhead (Idol et al., 2012, Page 809) - the phenomenon is known as "lift" or "drive" (Sills, 1993). Brine (salty) water in the well can also contribute to lift, as it expands slightly as the well loses pressure during hydrocarbon production.

Table 2 : Typical Composition for Types of Oil and Gas Well (Whitson and Brule, 2000, Table 2.1)

Hydrocarbon Species	Black Oil (mol%)	Volatile Oil (mol%)	Near-Critical Oil (mol%)	Gas Condensate (mol%)	Wet Gas (mol%)	Dry Gas (mol%)
C1	34.62	58.77	69.44	73.19	92.46	86.12
C5 plus C6	~2.25	~3.67	~3.49	~2.41	~0.35	~0.5
C7+	56.40	21.76	10.04	8.21	0.82	0.00
GOR	300	1,490	3,650	5,450	105,000	infinity

C1 = 1 Carbon atom per hydrocarbon molecule = Methane (CH₄);

C2 = 2 Carbon atoms per hydrocarbon molecule, etc.

C5+ = 5 Carbon atoms or more per hydrocarbon molecule ("Pentanes plus").

GOR = Gas to Oil Ratio, measured in scf/STB (standard cubic feet to Stock Tank Barrel).

Condensate wells, or "wet gas", or "gas condensate" wells, are a quasi-liquid mixture of gas and oil, often under high pressure (Idol et al., 2012, Page 809; IEA, 2010b), and are frequently found in deeper locations than crude oil reservoirs, and correspond to later stages of kerogen catagenesis, when increasingly more gas is produced than oil. When the gaseous phase components are separated from the liquid phases, the resulting gas will have a significant fraction of hydrocarbons heavier than methane, in the form of vapour mixed in with the methane gas.

In "lean" or "dry" gas wells, there is very little in terms of heavier hydrocarbon vapour in the raw gas. This gas is referred to as "non-associated", or "gas well gas". Although the gas in dry gas wells may have migrated upward from source rock, some gas wells are very deep, and this corresponds to later stage catagenesis of kerogen, when very little oil is being made, at the expense of higher levels of gas produced.

Dry gas is also produced from coal seams ("coal seam gas" or "coalbed methane" (CBM)) that have passed through the gas window for humic kerogen. This is one of several sources of gas known as "unconventional gas".

Dry gas is also produced from strata where there is low permeability, such as tight gas or shale gas. Tight gas is found in pores in sandstones and limestones, "tight sand"; and shale gas is found

in shales. Special drilling techniques, such as the use of hydraulic fracturing are necessary to liberate the gas to exit the well. These are known as "unconventional gas", or "non-conventional gas". There is also "tight oil" and "shale oil", preserved in its source rock, sedimented sand or shale.

Other sources of unconventional gas include methane hydrates, found at a particular depth, pressure and temperature on sub-sea continental shelves. It seems possible that this is composed mostly of "biogenic" than "thermogenic" methane.

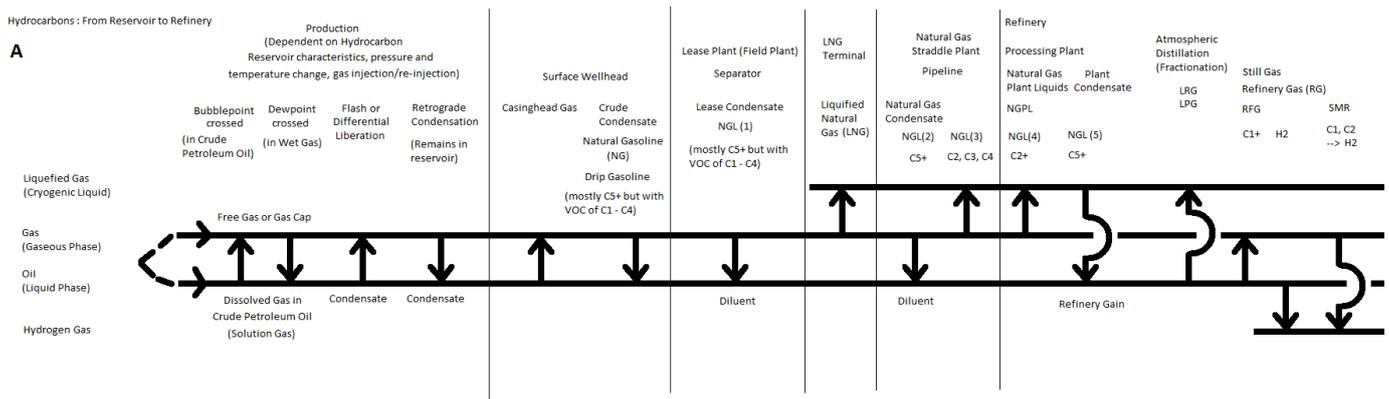
Recently, oil has been prospected from coal deposits, as there is also an oil window for humic kerogen, but with low production (Killops and Killops, 2005, Figure 4.20; Petersen, 2006).

1.2 Oil and gas processing

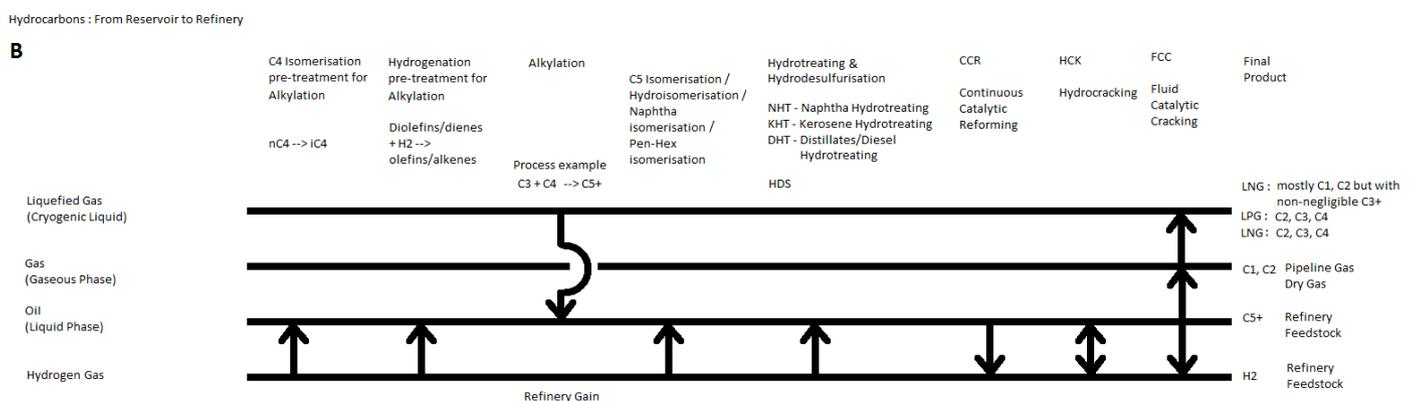
(see Figure 1)

Figure 1 Oil and Gas Processing

(a) From Reservoir to Refinery



(b) Refinery Processing and Hydrogen



1.2.1 The wellhead

In a hydrocarbon well where the liquids and gases are coming up from a reservoir at high pressure, at the surface, where the hydrocarbons emerge at the "wellhead", it is important to employ equipment composed primarily of chokes and valves - a "Christmas Tree" to control the flow of hydrocarbons coming out of the well, and enable the injection of chemical substances, water, gas or equipment into the well. This plant can be either on land, or under water, in the case of subsea drilling. It includes what is known as a "blowout preventer" (BOP), which is intended to prevent explosive escape of material from the well.

Where liquid and gaseous hydrocarbons are present together in a reservoir, depending on the reservoir temperature and pressure, some of the liquids may be vapourised in the gases, and some of the gases may be dissolved in the liquids. If gaseous and liquid phase hydrocarbons are emerging together from an onshore well, some of the gas may dissociate from the liquid in the equipment, and will either need to be vented, or removed for other purposes. This is known as "casinghead gas", or "oil well gas" and it is a mixture of gaseous phase hydrocarbons, the lowest molecular weight being methane, but it may contain a significant proportion of hydrocarbons with a molecular weight heavier than methane (Gurova and Kondratov, 2013; Medvedev and Kondrat'eva, 2008). If this gas is collected and compressed, liquid hydrocarbons can be condensed out, which may be known as "casinghead gasoline", or "natural gasoline" - a "condensate".

As gaseous phase hydrocarbons emerge from a deep onshore well under pressure and subterranean high temperatures, it will be cooler at the wellhead, and any release of pressure will also cool the hydrocarbon mixture. If there is a significant proportion of hydrocarbons heavier than methane and ethane in the gas, then these can condense out under these conditions. This is known by a variety of names, such as "wellhead condensate", "natural gasoline", "drip gas" or "white gas". It has a roughly similar chemical composition to other liquid hydrocarbons condensed out of Natural Gas, and if collected and compressed, can be put to use in the same way.

If a reservoir contains significant amounts of both oil and gas together, the liquid hydrocarbons and gas emerging from both onshore and offshore subsea wells (Rigzone, n. d.) will need to be separated, and this is done in the field where the well is drilled, using a Gas Oil Separator Plant (GOSP), or other "lease separator", such as a hydro-cyclone, which can remove any water directly, for example for well re-injection and stimulation purposes. If the hydrocarbon gas is surplus to requirements, this can also be reinjected in the well here. This equipment can also be designed to remove sand, sediment and other debris from the oil, condense the heavier hydrocarbon vapour out of the gas to a liquid form ("field condensate" or "lease condensate") and aim to remove as much of the water as it can ("dehydrator"). The liquids, which consist of crude petroleum oil and field or lease condensate will be destined for oil refinery, and the gases will be destined for gas processing plant, and each will be delivered by separate pipeline.

If there is any water left in the crude oil, emulsifiers must be used in the pipeline. To avoid the formation of plugging methane hydrates in a gas pipeline (should the gas continue to contain some water and then encounter low temperature conditions en route to the gas processing plant, highly likely if the pipeline is subsea), methanol can be added via a Chemical Injection Pump (CIP), such as in Canada, or the pipeline can be heated (Total, n. d.).

Small diameter "gathering" pipelines convey Natural Gas and crude oil at low pressure to gas processing plant and oil refineries, which are sometimes co-located. Where oil and gas are drilled

out at sea, their processing may be done at refineries located where the pipelines reach shore, or in some cases, on specialised ships.

1.2.2 The Natural Gas straddle plant

There may still be hydrocarbons with longer carbon chains than methane in the gas, so partway along a main onshore Natural Gas pipeline, there may be a straddle plant to remove them. More modern plant will use cryogenic techniques, and produce products for sale such as Liquefied Petroleum Gas (LPG) (see Table 3) and condensate, which may be called "Natural Gas condensate" (BP, 2006). Where the oil and gas is drilled subsea, it can be brought onshore for cryogenic separation (e. g. Apache, n. d.).

Table 3 : Gases and Liquids in a Modern Oil Refinery and Gas Processing Plant

Liquefied Natural Gas (LNG)	Liquefied crude Natural Gas, after some essential processing.
Liquefied Refinery Gases (LRG) and Liquefied Petroleum Gas (LPG)	<p>Refinery Gases are output from a number of oil refinery processing stages, such as atmospheric distillation in a fractionation tower. These compounds are in the gas phase, so they will have True Boiling Points below normal refinery operation conditions, so below around 0 degrees C. Gas separation may be done by liquefaction through cryogenic processes. Some of the shorter chain alkanes can usefully be used as refrigerants. Gas separation can also be done at higher pressures. Refinery Gases are feedstock from other units to the Gas Processing part(s) of a refinery, and are principally (EIA 2013a; PubChem n. d.; Inficon n. d.) :-</p> <ul style="list-style-type: none"> C1 : methane C2 : ethane, ethylene, acetylene (ethyne) C3 : propane, propylene, 1-propyne (propyne, methylacetylene), propadiene C4 : normal butane, normal butene (1-butene, 1-butylene), isobutane, isobutene (isobutylene), cis-2-butene, trans-2-butene, 1,3-butadiene (butadiene) <p>Olefins and diolefins are not present in the original crude oil, but they are frequently by-products of oil refining processes, such as Fluid Catalytic Cracking (FCC). The alkane methane is rejected and usually added to the dry gas stream intended for pipeline gas. It may also become a petrochemical feedstock, or be used for fuel gas in the refinery - known as Refinery Fuel Gas (RFG). The alkane ethane is sometimes rejected and added to the dry gas stream intended for pipeline gas. It is usually taken to become a petrochemical feedstock, for example in the manufacture of plastics, or it may be used for fuel gas in the refinery, together with methane - known as Refinery Fuel Gas (RFG). The branched alkane isobutane can be taken off to be used as a feedstock in the alkylation of fuel additives at the refinery. The olefins/alkenes ethylene, propylene and butylene (butene) can be taken off to be used as a feedstock for alkylation for fuel additives. The diolefin (diene) butadiene can be taken off to be used as feedstock for alkylation for fuel additives. The olefins/alkenes ethylene, propylene and butylene (butene) could be taken off to be used for petrochemicals, for example in the manufacture of plastics (NZIC, n. d.).</p>

The olefins/alkenes propylene and isobutylene (isobutene) could be taken off to be used for petrochemicals, for example in the manufacture of elastomers (synthetic rubbers) (Plunkett's 2009).

The diolefin (diene) butadiene could be taken off to be used for the manufacture of elastomers (synthetic rubbers).

Any remaining alkynes and diolefins (dienes) will be rejected. This will be mostly MAPD (Methylacetylene - Propadiene), but could include acetylene (ethyne), propyne (methylacetylene), butadiene.

Normally, part of the processing will endeavour to recover any "Pentanes plus" (C5, C6 and so on) to recycle into the oil refinery, or for use as petrochemical feedstocks.

The remainder will be mostly C3 and C4 hydrocarbons, and principally propane, and will be marketed as Liquefied Petroleum Gas (LPG).

Natural Gas Plant Liquids

Hydrocarbon liquids produced from Natural Gas at gas processing plant, combined with Liquefied Refinery Gases from oil refinery.

Natural Gas Liquids

The total of Natural Gas Plant Liquids plus Liquefied Refinery Gases, minus the olefins/alkenes and diolefins (dienes).

The olefins/alkenes and diolefins (dienes) will generally be used for petrochemicals, be rejected, or be used for producing alkylates as fuel additives.

Hydrocarbon Gas Liquids (HGL)

A range of alkane and alkene hydrocarbons produced by oil and gas refinery. It is equivalent to Natural Gas Plant Liquids (NGPL) plus

Liquefied Refinery Gas (LRG).

It is also equivalent to Natural Gas Liquids (NGL) plus refinery olefin products (EIA, 2013b, Slide 4; EIA 2013a).

1.2.3 The gas processing plant

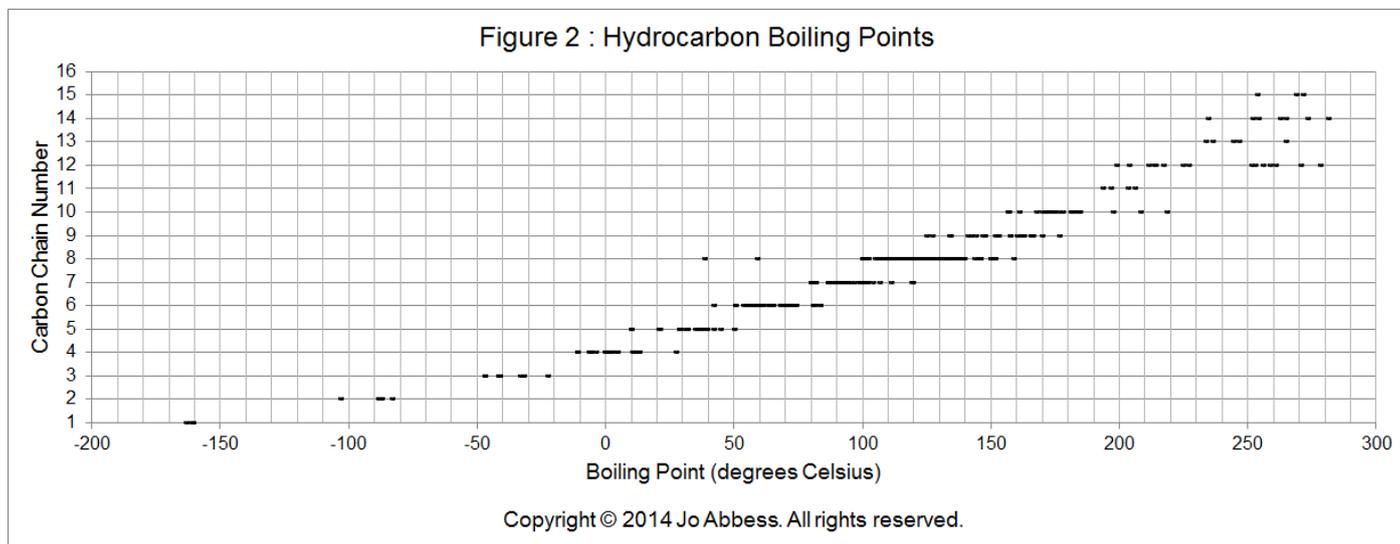
At the other end of the gas pipeline, at the gas processing plant, Acid Gas Removal (AGR) is a critical stage in the treatment of the wet gas, where hydrogen sulfide and carbon dioxide are removed. Nitrogen gas must be removed, then the mainly methane gas separated from any remaining heavier hydrocarbons in a "demethaniser". The remainder is fractionated into Natural Gas Plant Liquids (NGPL) (EIA, 2013b, Slide 4) - those gaseous constituents of raw gas that alter the heating value of Natural Gas : ethane, propane, butane, iso-butane; and "pentanes plus" - longer chain hydrocarbons, also known as "condensate" or "natural gasoline" (see Table 3). After the removal of the acid gases, and also after the removal of non-methane compounds, the resulting dry gas, with a very high percentage of methane, is ready for pipeline use, either provided to the gas grid or an oil refinery. The Natural Gas Plant Liquids (NGPL) are also useful in oil refinery.

1.2.4 The oil refinery

At the other end of the oil pipeline, at the oil refinery, the first main step is desalting and dehydration to remove particles of soil, sand, metals, salts and water from the crude oil (Moulijn et al, 2013, Section 3.2). The oil may need to be "stabilised", by having remaining gas and lighter hydrocarbons removed. Although there are many refinery configurations, the next main step commonly deployed is to pass the crude oil through a fractionator column for distillation at atmospheric pressure - an atmospheric distillation unit (ADU). The crude oil is heated to evaporation, but not combustion temperatures, and then the vapours are allowed to condense by fraction in a tower. The distillation fractions are separated by ranges of boiling points into major

cuts - mixes of hydrocarbons within a range (see Figure 2). "Light distillates" with light molecular weights include refinery gases, light naphtha and heavy naphtha, and these are used to make liquefied refinery gases (LRG) (see Table 3), and gasoline (petrol) products. "Middle distillates" are used to refine kerosene, diesels and light fuel oil. "Heavy distillates" are used to make heavy fuel oils, such as bunker fuel oil. The residual heavy compounds that emerge from the fractionator are known as "residua", "residuum" or "resids", and are used as feedstock to vacuum distillation units (VDU), which will give further light, medium and heavy distillates.

Figure 2 : Hydrocarbon Boiling Points



1.3 "Light ends" and refinery gases

By convention, the "light ends" of the distillation of crude oil are those fractions with a boiling point below that of cyclo-hexane (Jones, 2006). Hydrocarbons that remain in the gas phase at normal operation temperatures of the fractionator are composed of low molecular weight hydrocarbons : methane, ethane, propane and butanes. These are often known as "refinery gas" and have boiling points below around 0.0 degrees C. Gas processing at the refinery will generally be in operation to separate these. The methane and the ethane can be used as fuel gas at the refinery, or the ethane can be used in industrial chemistry, notably by "steam cracking" to ethylene (ethene), for plastics production, via polymerisation to polyethylene. If the refinery has processing that requires significant amounts of hydrogen, it will probably have a hydrogen plant, making hydrogen by the steam reforming of Natural Gas (SMR). In this case, the methane and ethane from the fractionated oil, could be used to supplement the Natural Gas supplied to the hydrogen plant. In most large refineries, there is cryogenic plant, and a portion of the "light ends" high in propane and butanes is chilled until it becomes liquid and becomes a refinery product known as Liquefied Petroleum Gas (LPG) (see Table 3). Propane is also an end product in itself. Isobutane (iso-Butane) can be used at the refinery for the production of alkylate used in gasoline blending, to raise the octane number and to produce a cleaner burn. Light ends gases are also becoming used as refrigerants (see Table 4) as apart from methane they have low Global Warming Potential (GWP) (Maclaine-cross and Goedhart, 1999).

Table 4 : Normal and True Boiling Points of Selected Hydrocarbons with 1 to 6 Carbon Atoms Per Molecule (C1 - C6)

(a) Light Hydrocarbon Gases

	Refrigerant (ASHRAE, 2013)	Experimental (ChemSpider, 2014)	Experimental (HSDB, 2014)
Methane	R-50	-164 degrees C (Oxford n. d.)	-161.50 degrees C (Haynes, 2013)
Ethane	R-170	-89 degrees C (Oxford n. d.) -88 degrees C (SynQuest n. d.)	-88.6 degrees C (Haynes, 2013)
Propane	R-290	-44 degrees C (NIOSH) -44.5 degrees C (Oxford n. d.)	-42.1 degrees C (O'Neill, 2001) at 1 atm
n-Butane (straight chain, normal Butane)	R-600	-0.56 degrees C (NIOSH) -1 to -10 degrees C (SynQuest n. d.)	-0.50 degrees C (Haynes, 2013)
iso-Butane (2-Methylpropane)	R-600a	-11.67 degrees C (NIOSH) -11.7 degrees C (Oxford n. d.)	-11.7 degrees C (Lide, 2005)

(b) Liquefied Light Hydrocarbons

	Refrigerant (ASHRAE, 2013)	Boiling Point/Boiling Range
Liquefied Petroleum Gas (LPG)	R-436A	-42.1 degrees C (Linde, 2010) -34.3 degrees C (Lad and Kapadia, 2014)

LPG is mainly Propane, iso-Butane (Isobutane), and sometimes also n-Butane (normal Butane) (Petrauskas, 2008).

(c) Light Naphtha Cut

Predominantly pentanes and cyclo-pentanes (Jones, 2006, page 189)

	Experimental (ChemSpider, 2014)	Experimental (HSDB, 2014)
n-Pentane (straight chain, normal Pentane)	36.11 degrees C (NIOSH) 35 to 36 degrees C (Oxford n. d.) 36 degrees C (Alfa Aesar n. d.)	38.06 degrees C (Haynes, 2013)
iso-Pentane (2-Methylbutane)	28 degrees C (Oxford n. d.)	27.8 degrees C (Lide, 2005) at 760 mm Hg
neo-Pentane (2,2-Dimethylpropane)	9.5 degrees C (SynQuest n. d.)	9.5 degrees C (Lewis, 2001)
cycloPentane	47 to 49 degrees C (Alfa Aesar n. d.) 49.44 degrees C (NIOSH) 49.00 degrees C (Oxford n. d.) 50.00 degrees C (SynQuest n. d.)	49.2 degrees C (Haynes, 2013) at 760 mm Hg

"reformat". Hydrogen gas is recoverable from the catalytic reforming process stage, which is operated either at high pressure or low pressure. Catalytic Reforming (CCR) is the source of the majority of refinery hydrogen (de Klerk, 2008, Chapter 4, Page 87, Footnote q; EPA, 2010, Section 2.2.5). Hydrogen can also be recovered from the hydrotreating process stages (Rabiei, 2012).

1.4.2 Middle Distillates : Hydrotreating

Feedstocks used for producing kerosene (jet fuel) and various grades of diesel vehicle fuel are generally hydrotreated with hydrogen gas (KHT, Kerosene Hydrotreating; or DHT, Diesel Hydrotreating). Hydrogen can be recovered from the purge gases (Schendel et al., 1983).

1.4.3 Heavy Distillates, Vacuum Distillation Gas Oils and Residua : Hydrotreating and Fluid Catalytic Cracking

Heavy molecular weight hydrocarbons, such as heavy atmospheric fractionator distillates, and light (LVGO) or heavy gas oils (HVGO) from vacuum distillation in a vacuum distillation unit (VDU), and residual unfractionated crude oil (Petti et al., 2006), may be subject to high pressure or low pressure hydrotreating (or hydroprocessing) using hydrogen gas. This is to prepare them to be fed into a Fluid Catalytic Cracking (FCC) unit to crack the longer chain hydrocarbons. Amongst other effects, hydrotreating will remove sulfur compounds, and help with the production of ultra low sulfur fuels (Stratiev et al., 2012). The Fluid Catalytic Cracker (FCC) will produce light cycle oil (LCO) that can be fed into the light distillates refining stream, and heavy cycle oil (HCO) that can be fed into the middle distillates refining stream. It will also produce de-sulfurised heavy fuel oil as a residue. Hydrogen can be recovered from the Fluid Catalytic Cracker (FCC).

Heavy molecular weight hydrocarbons, particularly if they have significant proportions of cyclic aromatics, or have already been through other processing (Moulijn et al., 2013, Section 3.4.5.2) can be treated with a Hydrocracker (HCU, HDC or HDCK) that uses hydrogen gas to "crack" the carbon chains resulting in lighter hydrocarbons that can be recycled into other refining stages, whilst suppressing olefin formation (Wang et al., 2004, Section 4.2.7). Hydrogen can be recovered from the hydrocracker (Davis and Patel, 2004).

Hydrogen gas can be recovered from visbreakers (viscosity reducer units), delayed cokers and flexicokers, which take heavy vacuum distillates and vacuum distillation residua to produce lighter hydrocarbons. Since there will always be a light gas fraction output from any thermal treatment of crude oil or its fractions, a proportion can be expected to be hydrogen gas, if the processing temperatures are high. Generally, even if there is not much hydrogen emerging, methane and ethane will be part of the off-gas, which can be steam reformed for hydrogen.

1.4.4 Other oil refinery processes that use hydrogen

Other processes in an oil refinery also use hydrogen gas. For example, in the gas separation section of the processing of light refinery gases, a C4 isomerisation unit to convert normal butane into isobutane. To top up feedstocks to the acid "reaction" stage of an alkylation unit, a hydrogen gas input will be needed to inhibit olefin formation (SET Laboratories, 2008), although the hydrogen can be recovered. A C5/C6 isomerisation unit preparing feedstock for gasoline blending also needs hydrogen, but can also recycle it.

The use of hydrogen gas in the catalytic dewaxing of diesel fuels and hydrocarbon oils used for machine lubrication is necessary to improve low temperature performance (cold flow properties). It can be anticipated that as more fuels are made from immature hydrocarbons, such as oil shale,

that this process will become more important and more hydrogen will become required in oil refineries (Gorring and Smith, 1979; Ward and Carlson, 1989).

Processing with hydrogen gas is also increasingly necessary for processing very heavy crude oils and tar sands oil. For example, hydrotreating is used to remove sulfur and nitrogen compounds from hydrocracked bitumen (ExxonMobil, 2011, Slide 8) in order to produce a freely flowing pipeline product known as syncrude; and the hydroconversion of heavy crude oils is expected to become important (Ghane and Khorasheh, 2014).

1.5 Cross-linking between oil and gas refinery

The light ends from an oil refinery atmospheric pressure distillation unit fractionator (ADU) will be essentially the same constituents as in lease condensate (field condensate), "pentanes plus", - hydrocarbons with a carbon chain backbone of more than five atoms, plus some light gases - methane, ethane, propane and butanes. Refinery offgas from various other refinery units will be the lighter gases - mostly paraffins (alkanes, or straight chain hydrocarbons), but it will also have some olefin components (alkenes, or hydrocarbons with doubled carbon-carbon bonds). Together, when stored as liquids, these are reported as Liquefied Refinery Gases (LRG). In a gas processing plant, condensable gases will be taken out of wet gas, and these are known as Natural Gas Plant Liquids (NGPL). Chemically, NGPL is almost the same as lease condensate, and apart from the olefin components in LRG, NGPL is virtually the same as LRG. Oil and gas from the same field often appear on the same corporate quarterly and annual reports, even if they are processed in different places. To prevent anomalies in reporting and accounting for the quantity known as Natural Gas Liquids (NGL), the Energy Information Administration has proposed that the totals of oil refinery LRG and gas processing plant NGPL combined be known as Hydrocarbon Gas Liquids (HGL), and that the fraction remaining after removal of the olefins from the sum total of HGL should be the definition for Natural Gas Liquids (NGL) (EIA, 2013b, Slide 4).

1.6 The rising proportion of Natural Gas Liquids and the balance of light and heavy hydrocarbons

Although only a part of the various members of the condensate family - Natural Gas Liquids, Natural Gas Plant Liquids, lease or field condensate, Natural Gas condensate, natural gasoline (drip gas) and so on - can be used in the production of gasoline (petrol) or diesel fuel, the volume of NGLs is included in most reports for total world petroleum liquids production (BP, 2014c). The growth in the production of NGLs somewhat compensates for what some call a plateau in crude petroleum oil production, as some fields begin depleting, and as geopolitical and economic disturbances interfere with production, refining and distribution of fuel. The reason why the production of NGLs is increasing stems essentially from the following factors: the increasing scale of Natural Gas development; the increased use of associated gas; deeper oil wells producing more wet gas; and more dry gas well drilling (IEA, 2010b). As less Natural Gas is flared or vented, and more is added to the overall energy system, the corresponding NGLs will enter the supply of resources to refineries and plant. At the same time, more condensate wells are anticipated, as oil and gas drilling goes deeper. In the United States in particular, the growth in shale/tight gas drilling is bringing much more dry gas into the market. More NGLs will shift the balance of the spectrum of hydrocarbons in refinery towards the low end of the "light ends".

This change in the supply of hydrocarbons has implications for the ability of refineries to produce higher carbon chain compounds for fuel blending. The argument to move a significant proportion of heavy goods vehicle (HGV) fleets over to compressed Natural Gas (CNG) or hydrogen fuelling could be supported by projections of increasing volumes of Natural Gas and lighter hydrocarbon feedstocks. Gasoline, diesel and jet fuel production could be severely impacted as developers

reach for geologically deeper hydrocarbons which are more in the gas window than the oil window, and unconventional resources of gas. The deeper the fossil fuels, the more likely they are to have aged, or be thermally broken down, and the greater the likelihood of mining gas rather than oil. Unconventional liquid fossil fuels may be sourced from immature kerogen, or overly mature kerogen, and these too will tip the compositional balance of the crude oils that enter refinery. As well as the lighter oil that can be produced from the immature kerogen in oil shales, some players in the oil and gas industry want to exploit the heavier end of the spectrum of crude petroleum grades, such as "initial oil" and "kerogen residue" bitumen from tar sands, Latin American heavy oil, and extra heavy oils.

Crude oil suppliers have been offering blends and synthetic crudes for some time to balance the over-light and over-heavy resources. However, it is possible that a gap in the supply of middle distillates could emerge - the jet fuel and diesel fraction - which would require intervention, as air travel is booming, and demand for diesel vehicle fuel is expected to grow owing to agreements between the petroleum industry, vehicle manufacturers and government regulators. To take the lighter fractions of crude up to the naphtha and distillate fractions via chemical processing, and to take the heavy crude fractions down to naphtha and distillate fractions will require much higher utilisation of hydrogen gas in refining. Although some hydrogen can be recovered from some refining units and recycled, overall the "hydrogen pinch" analysis is likely to suggest a greater call for fresh or make-up hydrogen. Although the steam reforming of Natural Gas is an obvious choice for hydrogen plant, particularly as some of the refinery gas feeds can be added to it (principally C1 and C2, methane and ethane), it cannot be assumed that Natural Gas will stay inexpensive enough to keep production margins stable, as demand for Natural Gas outside the oil refinery will become increasingly stronger. An added complication is that steam reforming of Natural Gas is perhaps the largest source of carbon dioxide emissions in an oil refinery (Sayles et al., 2011).

The other implication arising from greater NGL production is that there could be increasing amounts of undemanded light refinery gases. Although there should continue to be a strong market for iso-butane, for alkylate production as a fuel improver, other markets would need to be developed for the other C2 to C4 carbon chain compounds.

Whichever route is taken as regards fossil hydrocarbon resources, there will be a large investment requirement in new oil and gas refining plant, and there will inevitably be a growing need for hydrogen. Making the best use of heavier hydrocarbons will almost certainly require the use of "carbon rejection" units, such as partial oxidation or gasification, which will produce solid carbon coke or carbon dioxide gas as unwanted by-products. Coke would probably then be gasified, which would produce more carbon dioxide. Furthermore, an alternative to using Natural Gas for the production of hydrogen in a refinery would be the partial oxidation or complete gasification of coal, which would also produce coke and/or carbon dioxide. Any of these carbonisation routes imply greater carbon dioxide emissions, and breach strict climate controls.

Moving away from heavier hydrocarbons, and leaning towards using lighter hydrocarbons in future oil refining will perhaps require a change in focus towards the production of gaseous phase fuels (CNG, hydrogen etc) for transportation in addition to alternative liquid fuels (LPG, DME etc). In addition, car manufacturing and marketing strategies would need to change alongside any movement in fuel choices. Distillates may become increasingly targeted towards jet fuel production, as there may be no adequate substitution for this for aeroplane engines/turbines.

Besides carbon dioxide there are other pollution questions arising from changes in the "crude slate" - for example, the delivery of Canadian syncrude to the United States of America has been

beset with accident and tragedy, and the evidence so far shows that neither train nor pipeline can resolve the risks of transporting these highly toxic, highly polluting substances.

Petrorefinery is already in a state of change - for example, innovative uses of heavy hydrocarbon residue from refining heavier oils will need to be found, as it will probably not be possible to turn all of this into fuel as the market for heavy fuel oil is set to reduce, owing to air quality and climate change policy.

1.7 Light and heavy crude oil blends will increase refinery "churn"

In the United States of America, where there has been a focus on the production of light tight oil (LTO), there is an imbalance, as oil refineries are often designed to take heavier crude. This perhaps partly explains the drive to import heavier blends or synthetic crude oils from Canada. It is expected that crude oil producers will improve their blends. However, although this blending of feedstocks can balance out the overall slate of crude yields, besides requiring the crude producer to expend more energy in tailoring the blend, it implies increased oil refinery processing, both at the light and heavy ends. At the heavy end, more catalytic cracking and hydrocracking will be required, and at the light end, more isomerisation and alkylation. In addition, more hydrodesulfurisation will be necessary due to the potential for a higher level of sulfur in heavier oils, a trend also compounded as a result of tighter sulfur emissions control regulation. This will inevitably mean that the EROI or EROEI - Energy Return on (Energy) Invested - the ratio of produced energy to the energy used in processing - will decrease. This may well cancel out the economic benefits of using cheap crude oils in the heavier categories, even in blends with lighter oils.

1.8 Environmental and health shifts

The demand for the refinery product heavy fuel oil (HFO) is set to reduce, both for power generation and shipping transportation, and this means that refineries need to re-balance their heavy ends processing, and this is resulting in more feedstock for FCC, which in turn means more feedstock for gasoline blending. This influences the ratio of gasoline to diesel production, and could be a factor should there be a transport policy decision to stem the "drift to diesel" and promote "go for gasoline" - for example in electric/petrol hybrid vehicles. Furthermore, there are increasing concerns about diesel from an air quality point of view. Medical research studies have tentatively causally linked diesel exhaust particulates to asthma attacks, autism and more certainly to cancer. But petrol-gasoline is also not free from impact. High levels of aromatic hydrocarbons in gasoline are legislated against, partly because of the risk of exposure to carcinogenic aromatics such as benzene which can cause DNA methylation and lead to cancer. Burning hydrocarbon fuel, whether gasoline or diesel, can produce Polycyclic Aromatic Hydrocarbons (PAH), such as benzopyrene, which has been shown to be carcinogenic, and have other health impacts. Urban air quality statutes are likely to lead to an increased market for catalytic exhaust converters, and lighter, lower-carbon and carbon-free vehicle fuels, such as LPG, CNG and electricity. This would buck the trend towards sourcing heavier crude oils for refining, and would enable greater use of lighter oils and condensate. This would necessitate investment in new refinery plant for countries such as the USA, as well as new vehicle manufactory.

1.9 Peak Sweet

A shift away from conventional low-sulfur "sweet" and light crude oils has led to a range of adaptational responses in refinery, particularly with a view to meeting future transportation needs. Most additional processing in oil refinery risks losses in profitability, even when sourcing cheaper

crudes, as these can be more sour crude - with higher sulfur compounds - and heavier - which can mean smaller volumes of distillation fractions suitable for transport fuels.

In getting the crude oil out of the ground, "Peak Sweet" could perhaps become an indication of a peak in the rate of total liquids (and therefore the rate of refined products) that can be produced, as chemistry could be correlated to rates of production. "Peak Sweet" is a result of producing depleting old fields together with more complex new fields, with worse reservoir characteristics and production parameters - and a group of heavy/sour fields and old fields may be slower to produce than one large sweet/light one. Assessments of total economically recoverable hydrocarbons from a province does not usually include a projection of the rate of recovery, but watching the indicators for light, sweet crude percentages could offer a proxy.

While it is true that formerly uneconomic resources could become economic in future, and correcting former defects in categorisation can lead to more reliable reserves growth figures, the prevailing questions are : how much energy a producer (or refiner) needs to expend to return one unit of usable crude (or fuel), and how long it takes to do it. Profit margins could be crushed by a number of factors, and the complexities of refining and the imbalances caused by changing feedstocks could lead to a situation of unmet demand. The potential fall in energy gain from energy spend (EROEI or EROI) in petrorefinery from using lower grade crude oils, the increased need for hydrogen for processing, and the increased need for carbon disposal without causing greenhouse gas emissions are the three main factors that could cause refined petroleum oil products to rise in manufacturing cost after "Peak Sweet" is encountered. These would be real cost increases, and not a by-product of market speculation.

1.10 The lean towards hydrogen

Much hydrocarbon processing is either "hydrogen addition" or "carbon rejection" (Castaneda et al., 2014; de Klerk, 2008), decreasing or increasing the number of carbon-to-hydrogen bonds in hydrocarbon compounds in order to meet different criteria, such as raising the octane number of blended gasoline to reduce engine "knocking", or thermally treating heavy residua to obtain more useful feedstocks via cracking or coking. Using hydrogen in the chemical engineering of crude oil has become prevalent, and is making key processes environmentally safer and cleaner than other options. The trend in large refineries seems to be to use more hydrogen treatments as time goes by, and data indicates higher future hydrogen demand (e. g. Praxair, 2011). Although hydrogen can be recovered as well as consumed in several key processing units, the shift in the spectrum of hydrocarbon inputs arising from the mining of alternative fossil fuel resources could well lead to a large increase in demand for hydrogen.

Somewhere in the region of 41 to 54 million tonnes of hydrogen is produced globally each year : "merchant" for sale in general markets, and "captive" for use by its producers (DIS, n. d., Table 1; Evers, 2008a; Gupta, n. d.; Linde, 2007). Oil refining consumes roughly 25% to 35% of all hydrogen produced around the world, whilst ammonia production (principally to make fertilisers) consumes over 50%, and the rest of the chemical industry roughly 10% to 15%. In North America, where a wider spread of lighter/heavier hydrocarbons are in use for oil production, roughly 60% of all hydrogen used is consumed in oil refinery (Evers, 2008b). Of the American States, Texas, California and Louisiana consume the most hydrogen for oil refinery (DIS, n. d., Figure 13). In Canada, in 2010, roughly 23% of all hydrogen consumed was for the purpose of heavy oil upgrading, and 24% for oil refining (Dincer and Zamfirescu, 2011, Figure 1.3; Naterer et al., 2013, Figure 1.3). Hydrotreating in US oil refineries appears to be rising sharply. In 2004, roughly 14 million barrels a day of crude oil product was hydrotreated, and in 2030, this could rise to 27 million barrels a day (Karatzos et al., 2014, Pages 47 - 48, Section 1.10 and Figure 1-18).

Hydrogen production capacity increased by around 15% between 2003 and 2006, much of this to meet needs in oil refinery and hydrocarbon distribution systems (Evers, 2008a). A large new market for hydrogen could emerge in China, as the country applies a range of methods to address air pollution from transport and power generation.

1.11 Manufactured crude

The chemical processing of raw crude oil has becoming increasingly complex over the decades, and with the trend towards cheaper, heavier, lower quality and sour crude oil stocks, there will be economic benefits should crude oil producers partially process their raw crudes before supplying them to oil refineries. This is already happening with North American crude oils supplied to the United States of America by Canada, for example. There is likely to be a rising demand for blended crudes and synthetic crudes, tailored to end use refinery needs, for example, in blending condensate exported from the USA to Canada, with heavy Canadian crude oils in Canada, for re-export to the USA (Wood Mackenzie, 2014). To some extent, this means that even before the crude oil reaches the oil refinery, it is already no longer "Natural Crude", it is a manufactured product. With the increasing trend for hydrogen to be used in oil refinery processing, it is apparent that here too, both the feedstocks and the end products are no longer "Natural Petroleum", but rather, engineered. For example, although there is sufficient light naphtha available from all refinery units to the gasoline pool for blending, there is less "straight run" feedstock from atmospheric pressure distillation (ADU) that isn't post-processed.

This is important to consider, as this is almost the reverse of the shift from using manufactured oils over to using crude petroleum oil that took place in the early part of the 20th Century. In particular, the accelerating use of hydrogen in the chemical processing of crude oil has a very pertinent parallel with the need for hydrogen in the manufacture and processing of Renewable Gas from biomass and recycled gas feedstocks. Already, oil refineries employ gasification, one of the key technologies for Renewable Gas, especially for dealing with high hydrogen demand and disposing of high levels of residue from heavier crudes. For example, ExxonMobil's Flexicoking process has a gasification reactor to produce a hydrogen-rich gas (ExxonMobil, 2011, Slide 13); Foster Wheeler have developed the PetroHyPower unit that also uses gasification for hydrogen and power production (Foster Wheeler, 2013); and Shell's Gasification Process (SGP) uses carbonisation, or partial oxidation (POX), to produce hydrogen and power (Higman, 1994). With an increasing demand for hydrogen, perhaps hydrogen production could become the core of processing for "manufactured crude" (Chen 2001; Chand, 2002; de Klerk, 2008); however increased carbon dioxide emissions would need to be avoided. One way to approach this would be to maximise the energy gleaned by recycling the carbon dioxide (e. g. Lanzini et al., 2014).

For the time being, lighter crudes, blends and synthetic crude oils, coupled with increased hydrogen-based processing, could answer demand for gasoline and diesel, but if they become "missing fractions" from the blended or pre-processed crude oils, it will be hard to compensate without major innovation, as excess refinery hydrogen plus excess refinery carbon do not add up to distillates. It could be that the fossil fuel energy companies, instead of entering a permanent decline, decide to develop Renewable Hydrogen, Renewable Methane and Fischer-Tropsch liquid biofuel production, as a bridge to manufacture a new relevance for themselves as the 21st Century progresses.

2 The chemistry of Renewable Gas

The initial aim in developing resources of sustainable and renewable resources of gas - principally Renewable Hydrogen in the first instance, followed by Renewable Methane - is twofold : to compensate for degradation in the quality of fossil fuels, and to prevent greenhouse gas emissions of carbon dioxide or methane from the production, processing or use of fossil fuels. The more long-term aim for Renewable Gas will be to compensate for decreasing supplies of fossil fuels.

2.1 Hydrogen production is vital

One of the most versatile and highly-used gas fuel compounds is methane (CH₄), made of molecules that have four hydrogen atoms bonded to a single carbon atom, and it has a high heat of combustion. Weight for weight, only hydrogen gas, composed of molecules of two hydrogen atoms bonded together, has a higher heat of combustion (McAllister et al., 2011). Most fossil and biomass fuels, when burned in pure oxygen or air (oxidised), produce quantities of carbon dioxide (CO₂) and small amounts of carbon monoxide (CO), molecules of a single atom of carbon bonded to either two or one oxygen atoms. The concept of returning "waste" carbon oxides to manufactured fuel after combustion of the original fuel can be known as "carbon recycling", and is one of the ways in which Renewable Gas can be made. If we want to recycle this carbon-rich "waste" gas, and turn it into new manufactured fuel, it is possible to restore combustion energy value by chemically reacting the carbon oxides with hydrogen gas (H₂) to form methane (CH₄). Alternatively, if the "waste" gas is high in carbon monoxide, which is in/flammable, a simple mixing with hydrogen gas will make a fuel suitable for some applications - commonly known as syngas. To increase the potential of Renewable Gas fuels made by recycling carbon-rich gases, it can be seen that is necessary to maximise the production of hydrogen gas, which is one of the reasons why a range of ways to increase the production of hydrogen are being developed. The hydrogen to carbon ratio in biomass is low (Kopyscinski, 2010, Section 2.1.1, "Chemistry and thermodynamics"), for example H:C = 5:3 in cellulose, so it will not be possible to recycle high levels of carbon without additional supplies of Renewable Hydrogen beyond the biohydrogen produced from biomass resources. For example, "steam" thermochemical treatments can incorporate more hydrogen into the equation from water.

2.2 Gasification and steam gasification

After complete combustion of carbon-rich fuels of all kinds, where adequate oxygen has been available, and the combustion takes place in an enclosed chamber, or reactor, most of the hydrogen will have been reacted with oxygen to form steam, which is vapourised water (H₂O) - one atom of oxygen bonded to two hydrogen atoms. The oxygen can come from the air, or other gases whose formulae contain oxygen, added to the fuel, or from compounds in the fuel (oxidants). The other major "exhaust" gas is carbon dioxide (CO₂) - one atom of carbon bonded to two oxygen atoms. The more efficient the combustion process, the more oxygen is incorporated, and the more the "off-gas" or "flue gas" will contain these two chemical species. In a reactor with less oxygen available, combustion is known as "gasification" or "partial oxidation". Rather than in the case of complete combustion, where carbon dioxide is formed, instead, because oxygen is restricted, carbon monoxide will be formed from the carbon - one atom of carbon bonded to one atom of oxygen. And instead of water being formed, hydrogen gas will be formed from the fuel - two hydrogen atoms bonded to each other. Importantly, if water is added to the gasification chamber in the form of steam, more hydrogen gas is produced as a result, through a cascade of reactions. In effect, the steam gasification of fuels enables the liberation of hydrogen gas from water.

2.3 The biological, thermochemical and electrochemical decomposition of biomass

Most carbon-rich fuels originate from plants : where they are from ancient geologically altered sources they are known as fossil fuels, and when they are from recent surface sources they are known as biofuels (if liquid) or biogas (if gas). The energy from recently living plants is known as bioenergy, and the material used to produce biofuels is known as biomass. Both fossil fuels and biomass can be thermochemically treated, or gasified, in the same way, but there are important differences. Because biomass has more volatile hydrogen-rich components than coal, for example, which rapidly leave the material upon heating, and the carbon-rich residue that is left by volatilisation is more reactive in biomass than in coal, as a result gasification of biomass can be done at lower temperatures (Klass, 1998, Chapter 9, Section IV). Biomass often has a high moisture content, and this is an important consideration for designing gasification processes.

Gasification is just one way in which Renewable Gas, and the important Renewable Hydrogen, can be produced from biomass. For example, Renewable Hydrogen can be generated directly from biological decomposition, although, generally more methane is produced than hydrogen. However it depends on a range of factors, including the levels of oxygen available to the microbiological organisms, the temperature and pressure of the reactor, and the species of microbes used.

Biogas could also be used to produce Renewable Hydrogen directly using electrochemical methods, by making it the input fuel to an internal reforming Solid Oxide Fuel Cell (SOFC) (Shiratori et al., 2010). Alternatively, biomass can be flash carbonised into biocoal, and used in a Direct Carbon Fuel Cell to produce carbon monoxide, which is then steam reformed to hydrogen and carbon dioxide - the "shift" reaction (see Table 9; Hemmes, 2010, Section 10.5).

Renewable Hydrogen can also be made from water, for example in a Solid Oxide Electrolyser Cell (SOEC) - a Solid Oxide Fuel Cell (SOFC) running in regenerative mode, or "in reverse" (Brisse et al., 2010); or a Proton Exchange Membrane Fuel Cell (PEMFC, PEM FC or PEFC).

2.4 The four key gases and the naming of things

There exists a plethora of special terminology for fuels and fuel processing, which necessitates further clarifications on nomenclature. The names of fuels, and the methods in which they are produced are critical to understanding Renewable Gas. Some outline naming conventions are suggested here (see Table 5; see Table 6; see Table 10) - but note that it does not cover all cases of gas fuel processing.

The convention adopted here is to name fuels that have been produced by microbiological decomposition of biomass with the prefix bio- at the front, such as biodiesel, biogas, biomethane, biohydrogen. If hydrogen (or methane) is produced from recently-living plants and animals, or their wastes, without recourse to microbiological activity, or is produced from inorganic matter, it is referred to as Renewable Hydrogen (or Renewable Methane). Gas production processes that use fossil fuels are said to produce Renewable Hydrogen (or Renewable Methane) only if the carbon dioxide emissions that would have otherwise resulted are permanently sequestered so that they cannot reach the atmosphere. The terms biosyngas and bioSNG modify the naming convention, as they may be made without the use of microbiological decomposition - however, the feedstocks for their production were produced this way, so they inherit the prefix "bio-". The term "Renewable Gas" further modifies the naming convention, as it is used as an umbrella or inclusive term to cover both gases from (micro)biological processes and from other chemical processes such as

thermochemical treatments. Importantly, it is used here as a term to encapsulate both hydrogen and methane produced in a renewable fashion - either as separate gases, or mixed.

Renewable Gas is at an interesting stage of development. It will be found that the terminology used by different engineering groups can be different. For example, some people refer to Renewable Gas as "Renewable Natural Gas", or "RNG", but that ignores the contribution that Renewable Hydrogen can make to the total production volumes. Other people refer to the renewable class of gas fuels as "RE gas" for "Renewable Energy Gas"; or to mean "Renewable Electricity Gas", meaning gas fuels that are created by using spare electricity production, but that is somewhat confusing, as it rules out gas fuels not created by overcapacity or excess generation in wind or solar farms. Yet others refer to all low carbon gas fuels as "green gas", regardless of provenance.

Importantly, there is often confusion about what is included in the category of syngas (synthesis gas, or SG), and what should be included in the category of SNG (Synthesised, Synthetic, Simulated, Substitute or Supplemental Natural Gas). The nature of thermal treatments of biomass means that depending on the feedstock, and depending on the temperature range of the process, the gas fuels that result have a range of chemical compositions – the more methane there is in the final product, the more likely it is to be called Synthetic Natural Gas, "SNG" rather than merely "syngas".

A simple rule of thumb for thermochemical treatments is that the lower the temperatures used for gasification, when technically it is known as pyrolysis, the results will have higher concentrations of methane, but also higher concentrations of contaminants, such as tars. This could possibly be referred to as "SNG", or "rich syngas", but it would need further processing to be acceptable for gas grid injection. Where high temperature gasification is used, this results in gas fuels with high levels of hydrogen and carbon monoxide and fewer contaminants, which are easier to remove. If it has any methane in it, the concentrations will be low. This output is almost universally known as "syngas", or "lean syngas", and if it is made from biomass, it is sometimes called "biosyngas" or "bioSG". "Syngas" or "biosyngas" is then in some cases put through a process of methanation to increase the levels of methane and make the gas fuel "grid ready". This product is usually called "SNG" or "bioSNG".

Table 5 : Renewable Gas terminology : some important processes (this list is not comprehensive)

Technique	Temperature, pressure, oxygen
a. Animal and plant waste	(Low concentrations of Biohydrogen produced)
a1. Anaerobic Digestion (AD)	Less than 65 degrees C, normal pressure, oxygen-free
i. Thermophylic (50°C–60°C)	
ii. Mesophylic (35°C–40°C)	
iii. Psychrophylic (15°C–25°C)	
a2. Advanced Anaerobic Digestion (AAD)	
i. Thermal hydrolysis (Cambi process)	Initial temperature 165 degrees C at high pressure
ii. Enzymic hydrolysis (Monsal process)	Over several days taking temperature from 42 to 55 degrees C, at normal pressure, oxygen-free
iii. Other methods of AAD	Acid/gas phased digestion, Three-phased digestion...
Pyrolysis/Torrefaction	Usually 400 - 650 degrees C, normal or raised pressure, oxygen-free
b. Organic & inorganic waste	(Medium levels of Biohydrogen or Renewable Hydrogen produced)
Gasification	Over 700 degrees C, high pressure, controlled oxygen The higher the temperature, the lower the methane content of the gas
c. Reactional chemistry	(High levels of Renewable Hydrogen produced)
Wind gas (Power-to-gas, P2G)	Electrolysis of water to hydrogen (H ₂) gas, normal pressure, oxygen a by-product
Catalytic hydrogen	Photocatalytic, electrocatalytic in water or acid, maybe raised temperatures (thermocatalytic), normal pressure, oxygen by-product

Table 6 : Renewable Gas terminology : some important product gases (definitions open to discussion)

Gas fuel	Principle chemical components
Compressed Natural Gas (CNG)	CH ₄ (methane), ethane, nitrogen, propane, CO ₂ (carbon dioxide), butane, ...
Liquified Natural Gas (LNG)	CH ₄ (methane), ...
Biogas or as Compressed Biogas (CBG)	CH ₄ (methane), CO ₂ (carbon dioxide), N ₂ (nitrogen), O ₂ (oxygen), ...
Biomethane or as Compressed Biomethane (CBM or BioCNG)	CH ₄ (methane), CO ₂ (carbon dioxide), ...
Biosyngas (BioSG) (syngas, SG, synthesis gas), ...produced by gasification at :- ~700 - 1000 degrees C ~1200 - 1600 degrees C	From gasification : contains about 50% of the energy value of Natural Gas H ₂ (hydrogen), CO (carbon monoxide), CO ₂ (carbon monoxide),Includes some CH ₄ (methane) and other hydrocarbons ...Includes insignificant CH ₄ (methane) or other hydrocarbons
BioSNG (Bio-SNG) (SNG, Substitute Natural Gas, Synthetic Natural Gas, Synthesised Natural Gas, Simulated Natural Gas, Substitute Natural Gas, Supplementary Natural Gas) Compressed BioSNG (CSNG)	From gasification, with additional processing : a closer match to Natural Gas; CH ₄ (methane), H ₂ (hydrogen), CO ₂ (carbon dioxide), ...
BioHydrogen (Biohydrogen bio-hydrogen)	H ₂ (hydrogen)
Renewable Hydrogen	H ₂ (hydrogen)

2.5 The chemical composition of gas

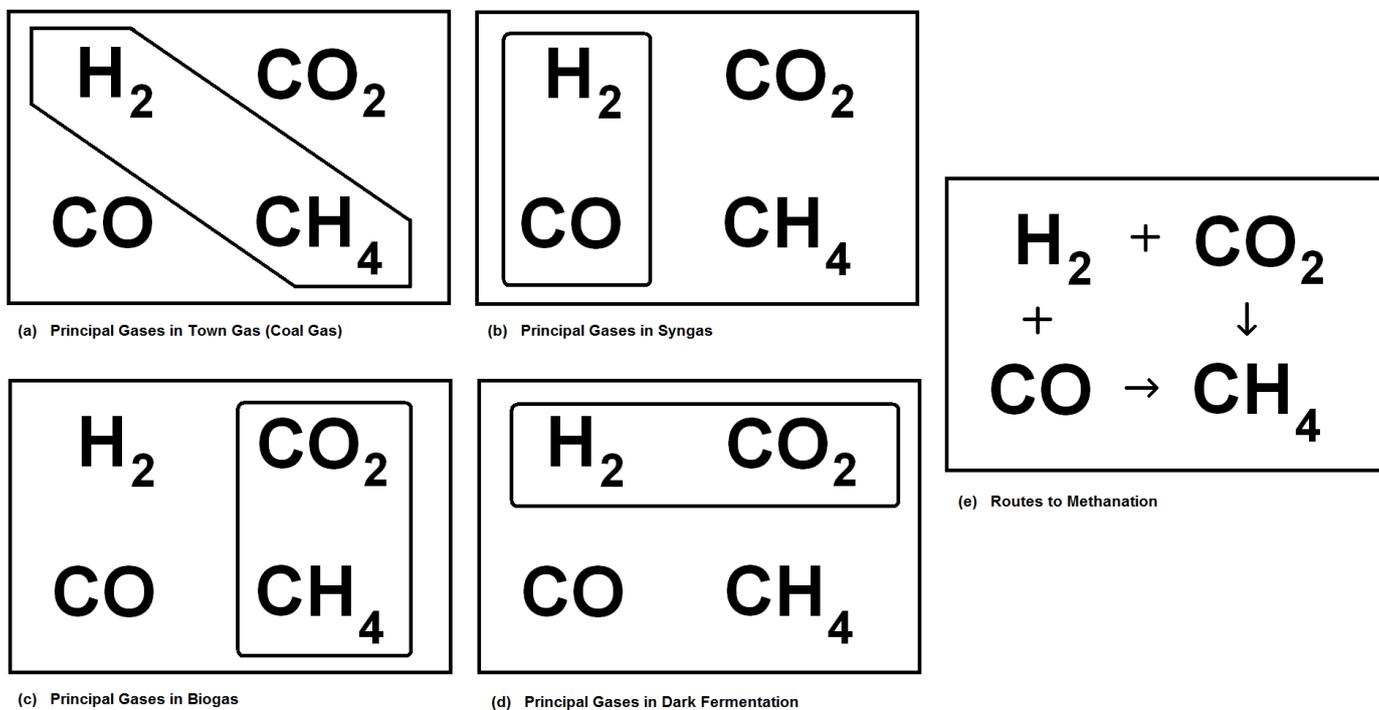
Table 7 shows rough approximations of the chemical composition of a variety of gases (see Table 7; Rojey et al., 1997). Note from Table 6 and Table 7 that four gases appear regularly : hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂) and carbon monoxide (CO) (see Figure 3). These are the key components of Renewable Gas chemistry. Note also that the gases appear in a somewhat different order of significance depending on the way they have been produced. This suggests that mixing Renewable Gas feedstocks could be a viable way to optimise the overall balance of the four main gases (according to requirements).

Table 7 : Approximate Representative Gas Chemistry

Type / Gas	Natural Gas	Gasified Biomass (Bio-Syngas)	Gasified Coal (Syngas)	Landfill gas (Biogas)	Digester gas (Biogas)
Methane	70% - 90%	3% - 11%	0% - 5%	35% - 65%	50% - 70%
Hydrogen	0% - 0.2%	5% - 26%	25% - 50%	0% - 3%	0%
Carbon monoxide	0%	13% - 27%	30% - 65%	0%	0%
Carbon dioxide	0% - 8%	12% - 40%	1% - 15%	40% - 50%	35% - 40%
Oxygen	0% - 0.2%	0% - 0.2%	0%	0% - 2%	0% - 1%
Nitrogen	0% - 5%	13% - 56%	1% - 3%	8% - 15%	0% - 5%

Syngas that has been produced at lower temperatures, or has been methanated, will have a higher methane content. In this case it would be generally referred to as SNG (or BioSNG in the case of biomass gasification).

Figure 3 Principal Gas Constituents and Routes to Methanation



2.6 The main Renewable Gas compounds

2.6.1 Hydrogen

Hydrogen gas was produced early on at an industrial scale via the "Water Gas" process, which was not renewable as it required the use of coke made from coal, although the hydrogen itself came largely from the steam deployed. Hydrogen gas in more recent decades has been made by the steam reforming of Natural Gas. Hydrogen is found in most fossil hydrocarbon sediments, but usually at low levels. High concentrations of fossil or "Natural Hydrogen" gas is sometimes found in places with unusual geology, and here is generally thought to be abiological in origin, through chemical processes involving rock and water that are continuous to the present day (de Marignan, 2013; Mayhew et al. 2011, 2013). However, these high-percentage hydrogen gas fields may be the result of specific colonies of microorganisms of very ancient lineage present in the material that was laid down in the strata, going through a process of chemosynthesis that favours hydrogen production rather than methane (Hellevang et al., 2011; Nisbet and Sleep, 2003; Nisbet and Fowler, 2011; Seth-Smith, 2007; Sherwood Lollar et al., 2006; Wu et al., 2005; Zahnle et al. 2013). Alternatively, it could be the result of severe cracking conditions of complex hydrocarbons at depth, pressure and temperature (Mokhatab et al., 2006).

Natural Hydrogen is not currently considered a significant source for exploitation, so renewable resources of hydrogen will mostly come from three other origins : the anaerobic digestion or fermentation of recently living biomass (co-produced along with methane); the gasification of biomass; or the separation of water into hydrogen and oxygen gas by photoelectrochemical, electrochemical, electrocatalytic, photoelectrocatalytic or other means. Processes being developed to produce hydrogen gas by the splitting of water frequently involve catalytic chemistry, as the bond dissociation energy of water is high (see Table 8). To make the distinction between these main forms of sustainable hydrogen, the term Renewable Hydrogen is used to refer to water splitting and biomass gasification techniques, whilst biohydrogen is used for hydrogen derived from organic material (biomass) via microbiological means.

Hydrogen gas can be used on its own as an energy fuel, but it can also be used in other gas mixtures. Methane-rich gas that has a certain proportion of hydrogen gas added to it has a greater combustion efficiency - the "hythane effect" (for example, Tunestal et al., 2004). Hydrogen gas is very helpful in building up the available volumes of Renewable Gas as it can be used in carbon recycling - the re-use of carbon dioxide and carbon monoxide gas, made into new methane gas fuel.

Hydrogen is altogether strange. It's not really a metal, but it often reacts like a metal. Hydrogen gas has a very low molecular mass and size, and this means it is rather more complicated to transport and store than some other gas fuels. There are currently proposals to carry a certain amount of hydrogen in the gas pipeline networks. The small molecular size theoretically permits hydrogen to pass through any lattice imperfections in the surface of metallic pipes and casings, which could cause embrittlement (Schmura et al., 2005), and risk the potential for rupture or cracking, although perhaps only high pressure sections of gas grids would need replacing for hydrogen to be distributed this way (Dodds and Demoullin, 2013, Section 2.2.1).

Besides compromising the integrity of metals, hydrogen can permeate through, or react with, a number of other materials. To add hydrogen to the gas grids in the developed world would require care - for example : pipe connectors and joints would need adjusting, old metal pipework would need to be checked for hydrogen leaks, and plastic pipe would need to be monitored for both rigidity and plasticity issues after exposure to hydrogen. A number of countries have already

undertaken tests to verify that the Natural Gas grid can take a proportion of hydrogen - including Germany, The Netherlands and Denmark, and the UK launched a test project in late summer 2012. In countries with programmes to replace local area low pressure metal gas grid pipelines with polyethylene plastic, hydrogen should not pose a problem (Iskov et al., 2010), although it is not yet known if hydrogen would affect the biopolyethylene that will need to be used in future.

Owing to its characteristics in general, storage of hydrogen is viewed as expensive - as metal tanks would need to be reinforced, and although there are ongoing research projects to find porous matrix materials that can soak up hydrogen like a sponge, these are not advanced, except for small-scale solutions using metal hydrides. The weight of hydrogen storage tanks is the main reason why mass deployment of personal hydrogen-powered vehicles could be unlikely - the mass of the vehicles would remove the efficiency advantage of using such a light and powerful fuel.

Hydrogen could be combusted with the methane-rich Natural Gas it is piped with, or it could be filtered out at the end point of use for specific purposes. It is conceivable that eventually the current gas grid could be used solely for the distribution of hydrogen gas (although this would require a change of end use appliances), if Natural Gas production declines and Renewable Methane and biomethane are all deployed elsewhere - in power generation and for transport needs. Small additions of hydrogen to the gas grid would displace fossil gas, but not significantly affect carbon emissions at the point of use. Because of this, methanation of the hydrogen is considered optimal by some before grid injection. A high percentage of Renewable Methane could be supplied by gas grids, as it is very similar to Natural Gas.

Hydrogen burns strongly in the presence of oxygen, so if a Renewable Gas has a high hydrogen percentage, it could need to have more "filler" (historically known as "ballast"), a less reactive or inert gas to balance the high rate of combustion of the hydrogen, to make it a manageable fuel. This will then reduce the energy density of the resulting gas.

Upgrading low-methane Renewable Gas to increase its internal energy value using the newly-produced Renewable Hydrogen is an attractive option - to avoid having the complications of hydrogen storage. If hydrogen is reacted with Renewable Gas, using methanation procedures, the resulting products will have a higher energy density, and be less complex to store safely.

Table 8 : Bond dissociation energy for selected compounds (Darwent, 1970)

	0 degrees K / -273.15 degrees C kJ/mol	298 degrees K / 24.85 degrees C kJ/mol
Hydrogen gas (H ₂)		
H ₂ --> H + H	432.00 +/- 0.04	435.93
Water (H ₂ O)		
H ₂ O --> OH + H	493.7 +/- 0.8	498.7 +/- 0.8
OH --> O + H	423.8 +/- 2.1	428.0 +/- 2.1
Carbon dioxide (CO ₂)		
CO ₂ --> CO + O	525.9 +/- 0.4	532.2 +/- 0.4
CO --> C + O	1071.94 +/- 0.4	1076.6 +/- 0.4
Carbon monoxide (CO)		
CO --> C + O	1071.94 +/- 0.4	1076.5 +/- 0.4

2.6.2 Methane

Methane is the simplest hydrocarbon and present in pretty much all fossil fuel deposits, including coal seams. The further down in the Earth's crust that petroleum oil and gas bearing formations have travelled, the higher the percentage is "cracked" by high temperatures to methane (thermogenic methane, see Table 10). Methane is a primary component of the off-gas from biological decomposition, and therefore the principle constituent (biomethane) of biogas made by anaerobic digestion of biomass (biogenic methane, see Table 10). This is a close parallel to Natural Gas, which is often something of the order of 75% to 85% methane. Methane is also a main constituent of the by-products of low- to medium-temperature gasification of biomass - although there are several drawbacks to this kind of production, including resulting in high levels of long carbon-chain hydrocarbon tars. The grid injection of biomethane (uprated or upgraded biogas) is already being done, but cleaning and upgrading the gas to grid quality remains energy- and resource- intensive. Methane is arguably much safer and cheaper to store than hydrogen gas, however it is highly volatile and explosive, so care is always needed. Having a higher molecular size and a higher energy density than hydrogen gas, the same amount of energy is in a carrier that takes up a smaller volume. This means that methane has a higher utility for gas fuel storage than hydrogen. If hydrogen gas is used to recycle carbon-rich gases, the most straightforward product of the various chemical pathways open to employ is methane, as it is the simplest hydrocarbon, does not include oxygen or nitrogen - which could affect equipment burning it - and is a gas at normal temperatures and pressures. A simple looping facility can be imagined, that uses excess wind power to split water to hydrogen gas, methanate the hydrogen gas with recycled exhaust carbon dioxide, store the Renewable Methane, and then combust it at times of low wind flow for electricity generation, and then store the output carbon dioxide for the next cycle.

2.6.3 Carbon monoxide, carbon dioxide

Until carbon recycling is ubiquitous, it may still be necessary to burn or gasify some fossil fuels. If fossil fuels are burned, the waste gas is mostly composed of steam (water) and carbon dioxide. If fossil fuels are gasified at high temperature, the result is syngas - synthesis gas - which is mostly composed of hydrogen and carbon monoxide. This is a useful fuel in itself, but separation of the hydrogen gas and carbon monoxide could be valuable. Despite some remaining questions about the exact mechanisms for catalysed gas reactions (Goodman, 2013), for example the hydrogenation of carbon dioxide (Wang et al., 2011), progress is being made on selective methanation, targeting either carbon monoxide or carbon dioxide, or both simultaneously (Probstein and Hicks, 2006), to make methane by reacting with hydrogen. The hydrogen can either be the hydrogen co-present in syngas or biogas, or additional hydrogen from other sources. Recycling the carbon oxides from the gasification or combustion of fossil fuels could become sustainable, requiring diminishing fossil fuel input and reducing the local environmental and atmospheric desecration from mining fossil fuels, so long as extra hydrogen gas and sufficient energy of reaction is provided to completely methanate the carbon-rich gas, according to the chemical reaction requirements.

2.6.4 Oxygen

Hydrogen is an important part of a Renewable Gas volumisation strategy, and there is a hidden bonus in its use. Splitting water not only creates hydrogen gas - it also liberates oxygen gas. If this oxygen is not used in subsequent processes, for example to optimise combustion, venting it to the atmosphere could begin to replenish atmospheric stocks, reduced by the burning of fossil fuels that has increased significantly since the start of the Industrial Revolution. The cost of filtering out pure oxygen from the air for energy and industrial purposes is high, so avoiding the need for an air separation unit (ASU) by electrolysing water for oxygen could be of benefit.

2.6.5 Nitrogen etc.

Outside biomethane and Renewable Methane, useful additional chemical products would be compounds such as biopropane, for a variety of chemistry and fuel applications. There are other potential elements of the suite of Renewable Gas chemistry, some of them not even in the gaseous phase - such as biomethanol and bioammonia. These would be made by chemical process engineering in a biorefinery. Besides its crucial use in oil refinery, a major use for nitrogen today is with hydrogen in the production of ammonia (NH₃) for formulating into agricultural fertiliser. The current process relies heavily on the gasification of Natural Gas, or coal (principally in China); so to grow carbon-neutral energy crops, the production of bioammonia for fertiliser is essential. For the Haber-Bosch process (or Haber process), nitrogen and hydrogen should be mixed to a specific ratio (N:H, 1:3) before being reacted together into ammonia. There are parallels between fossil fuel-derived ammonia production and some proposed industrial-scale processes for Renewable Gas production.

For typical "petroammonia" production (e. g. Linde, 2014; Moulijn et al., 2013, Figure 6.8), there are initially two reforming stages, and one (or rather, two) shift stages; and then there are two catalytic stages - in a reactor with a catalyst to promote the desired chemical reactions. Before the two catalytic stages there is a stage to remove carbon dioxide.

- (a) Steam Reforming of Methane (Natural Gas) : The first reforming stage is the steam gasification of already desulfurised Natural Gas - a high temperature treatment in an environment, medium, or atmosphere, of steam. This produces a syngas of hydrogen, carbon monoxide and some remaining methane.
- (b) Air Gasification : In the second reforming stage, gasification in an atmosphere of oxygen and nitrogen (both from air), and steam, reacts the remaining methane and produces a gas stream that is composed mostly of hydrogen, carbon monoxide and nitrogen.
- (c) Water Gas Shift : The chemical reaction known as the "Water Gas Shift" reaction (see Table 9) from its original historical use to convert "Water Gas", a syngas, to a high-hydrogen gas, is then deployed to react the carbon monoxide with steam, so that it forms extra hydrogen and carbon dioxide. The extra hydrogen needed for the ammonia synthesis reaction ratio is added through this processing in preparation for the final catalytic stage. This stage is conducted in two reactors, one at high temperature, and the other at lower temperatures.
- (d) Carbon Dioxide removal : The next process stage removes the carbon dioxide created during the Water Gas Shift stage, either through the use of Pressure Swing Absorption (PSA), or a chemical absorption method.
- (e) Carbon Monoxide Methanation : Next, the gas stream is passed through a catalytic Methanation stage, to convert any remaining traces of carbon monoxide to methane (see Table 9). Remaining carbon dioxide may also be methanated at the same time.
- (f) Ammonia Synthesis : Any steam is removed, and the final gas stream of hydrogen, nitrogen and a small amount of methane are passed through a second catalytic reactor. The hydrogen and nitrogen react to produce ammonia (see Table 9), and any remaining methane, which has been inert in the reaction, is recovered for cycling back to the start of the process.

The exact process conditions are controlled to make sure that the atomic ratio of hydrogen to nitrogen in the region of H:N = 3:1, the correct stoichiometric ratio for the ammonia synthesis reaction.

The gasification, "Water Gas Shift", or just simply "shift", absorption and methanation and synthesis elements of this process are standard in industrial chemistry, and so can be applied straightforwardly to the production of Renewable Gas. The gasification of biomass to produce syngas, could be followed by shift to produce Renewable Hydrogen, for example. Alternatively the gasification of biomass can be followed by methanation to produce Renewable Methane from the biosyngas. The carbon dioxide removal techniques can be applied where carbon dioxide needs to be captured from the combustion of fossil fuels and permanently sequestered so it cannot reach the atmosphere - Carbon Capture and Storage (CCS). The use of one chemical catalyst to promote methanation and another chemical catalyst to promote the reaction in the main ammonia synthesis stage is parallel to the usual requirement to use different catalysts for the methanation of carbon monoxide and for the methanation of carbon dioxide - the Sabatier reaction (see Table 9).

The Renewable Gas process would therefore be something along these lines :-

(a) and (b) Gasification of Biomass : This creates a syngas of hydrogen and carbon monoxide. In order to ensure high efficiency in conversion to syngas, the gasification reactor could need added oxidant gas, for example, air or steam injection. Carbon dioxide could also be used as a gasifying agent (e. g. Asadullah, 2014, Section 5.3; Jansen, 2011), but the exact choice of gasifying agents, or gasifying medium, would need to be chosen according to the nature of the biomass feedstock. The output would be mostly hydrogen and carbon monoxide.

(c) and (d) Water Gas Shift or Hydrogen Input : This stage would either deploy the Water Gas Shift or add in hydrogen gas from other sources. The Water Gas Shift would raise the carbon monoxide to carbon dioxide, at the same time producing extra hydrogen sourced from the reaction steam. Alternatively, Renewable Hydrogen could be added to the syngas. The output would be high in hydrogen, carbon dioxide and carbon monoxide. The carbon dioxide could be recycled to the gasification stage as gasifying agent.

(e) Carbon Monoxide Methanation (or "Methane Synthesis") : The first catalytic stage would methanate the carbon monoxide to methane, using some of the hydrogen. The output would be high in hydrogen, methane and carbon dioxide.

(f) Carbon Dioxide Methanation (or "Methane Synthesis") : The second catalytic stage would methanate the carbon dioxide to methane. The output would be high in methane. Some cleaning up stages would be necessary.

There are likely to be problems with this conceptual process, such as catalyst poisoning if the methanation stages are not done optimally. Also, the most efficient way to run this process could be by the addition of Renewable Hydrogen from other sources, rather than sourcing hydrogen from steam. If carbon dioxide were used as a gasifying agent, and it came from the burning of fossil fuels, or from industrial chemical processing of fossil fuel feedstocks, the resulting methane at the end of the process would therefore not be truly Renewable Methane.

Table 9 : Gasification Reactions (NASA CEA ThermoBuild, 2014)

(a) Reaction Number and Formula

Number	[Reactants --> Products]	Formula (Reactants --> Products)	
R1	[Gas --> Gas & Gas]	CO ₂	--> CO + 0.5 O ₂
R2	[Gas:Gas --> Gas & Gas]	CH ₄ + CO ₂	--> 2 CO + 2 H ₂
R3	[Gas:Gas --> Gas & Gas]	CH ₄ + H ₂ O	--> CO + 3 H ₂
R4	[Solid:Gas --> Gas]	C + CO ₂	--> 2 CO
R5	[Solid:Gas --> Gas & Gas]	C + H ₂ O	--> CO + H ₂
R6	[Gas --> Gas & Solid]	CH ₄	--> 2 H ₂ + C
R7	[Gas:Gas --> Gas & Gas]	CO ₂ + H ₂	--> CO + H ₂ O
R8	[Gas:Gas --> Gas & Gas]	CH ₄ + 0.5 O ₂	--> CO + 2 H ₂
R9	[Gas:Gas --> Gas & Gas]	CO + H ₂ O	--> CO ₂ + H ₂
R10	[Solid:Gas --> Gas]	C + 2 H ₂	--> CH ₄
R11	[Gas:Gas --> Solid & Gas]	CO ₂ + 2 H ₂	--> C + 2 H ₂ O
R12	[Solid:Gas --> Gas]	C + 0.5 O ₂	--> CO
R13	[Gas:Gas --> Solid & Gas]	CO + H ₂	--> C + H ₂ O
R14	[Gas --> Gas & Solid]	2 CO	--> CO ₂ + C
R15	[Gas:Gas --> Gas & Gas]	CO ₂ + 4 H ₂	--> CH ₄ + 2 H ₂ O
R16	[Gas:Gas --> Gas & Gas]	CO + 3 H ₂	--> CH ₄ + H ₂ O
R17	[Gas:Gas --> Gas]	H ₂ + 0.5 O ₂	--> H ₂ O
R18	[Gas:Gas --> Gas & Gas]	2 CO + 2 H ₂	--> CH ₄ + CO ₂
R19	[Gas:Gas --> Gas]	CO + 0.5 O ₂	--> CO ₂
R20	[Solid:Gas --> Gas]	C + O ₂	--> CO ₂
R21	[Gas:Gas --> Gas & Gas]	CH ₄ + 2 O ₂	--> CO ₂ + 2 H ₂ O

(b) Reaction Number and Name

Number	Reaction Name
R1	Thermal Cracking of Carbon Dioxide
R2	Carbon Dioxide Reforming of Methane
R3	Steam Reforming of Methane (SRM) : Steam Methane Reforming (SMR) : Steam Gasification of Methane
R4	High Temperature Boudouard Equilibrium Reaction : Reverse Boudouard Reaction : Carbon Dioxide Reforming of Carbon
R5	Water Gas Reaction (WGR) : Carbon-Steam Reaction : Steam Gasification of Carbon : Steam Reforming of Carbon
R6	Thermal Cracking of Methane : Carbon Deposition of Methane : Carbonisation of Methane
R7	Reverse Water Gas Shift Reaction (RWGS) : Reduction of Carbon Dioxide A
R8	Partial Oxidation/Combustion of Methane
R9	Water Gas Shift Reaction (WGS) : Shift Reaction : Steam Gasification of Carbon Monoxide
R10	Methanation 4 : Methanation of Carbon : Hydrogenation of Carbon : Hydrogenating Gasification of Carbon
R11	Reduction of Carbon Dioxide B
R12	Partial Oxidation/Combustion of Carbon
R13	Reduction of Carbon Monoxide
R14	Low Temperature Boudouard Equilibrium Reaction : Boudouard Reaction
R15	Methanation 3 : Sabatier Reaction : Methanation of Carbon Dioxide : CO ₂ Methanation
R16	Methanation 1 : CO Methanation : Methanation of Carbon Monoxide A : CO Hydrogenation
R17	Oxidation/Combustion of Hydrogen : Formation of Steam (Water)
R18	Methanation 2 : Reverse Carbon Dioxide Reforming of Methane : Methanation of Carbon Monoxide B
R19	Oxidation/Combustion of Carbon Monoxide :
R20	Oxidation/Combustion of Carbon :
R21	Oxidation/Combustion of Methane

(c) Enthalpy Change (delta H) at Temperature (degrees Celsius)

	delta H (kJ/mol)						
	525 deg C	575 deg C	605 deg C	655 deg C	675 deg C	725 deg C	825 deg C
R1	283.266	283.125	283.034	282.870	282.802	282.622	282.236
R2	259.085	259.407	259.543	259.676	259.701	259.689	259.395
R3	222.248	223.092	223.538	224.187	224.416	224.911	225.605
R4	172.359	171.970	171.722	171.285	171.105	170.636	169.646
R5	135.522	135.655	135.717	135.796	135.820	135.858	135.856
R6	86.726	87.437	87.821	88.391	88.596	89.053	89.749
R7	36.837	36.315	36.005	35.387	35.285	34.778	33.790
R8	-24.181	-23.718	-23.491	-23.194	-23.101	-22.933	-22.841
R9	-36.837	-36.315	-36.005	-35.489	-35.285	-34.778	-33.790
R10	-86.726	-87.437	-87.821	-88.391	-88.596	-89.053	-89.749
R11	-98.685	-99.340	-99.712	-100.307	-100.535	-101.08	-102.066
R12	-110.907	-111.155	-111.312	-111.585	-111.697	-111.986	-112.590
R13	-135.522	-135.655	-135.717	-135.796	-135.820	-135.858	-135.856
R14	-172.359	-171.970	-171.722	-171.285	-171.105	-170.636	-169.646
R15	-185.411	-186.777	-187.533	-188.698	-189.131	-190.133	-191.815
R16	-222.248	-223.092	-223.538	-224.187	-224.416	-224.911	-225.605
R17	-246.429	-246.810	-247.029	-247.381	-247.517	-247.844	-248.446
R18	-259.085	-259.407	-259.543	-259.676	-259.701	-259.689	-259.395
R19	-283.266	-283.125	-283.034	-282.870	-282.802	-282.622	-282.236
R20	-394.173	-394.280	-394.346	-394.455	-394.499	-394.608	-394.826
R21	-800.305	-800.463	-800.583	-800.826	-800.937	-801.243	-801.969

(d) Energy Balance of Reaction & Gibbs Free Energy Inflection (degrees C, approximate)

Endothermic (taking heat in) or Exothermic (giving heat out)		Spontaneity of Reaction		Gibbs Free Energy inflection point
Qualifier	Direction	Qualifier	Degrees Celsius (approximate)	
R1	Severely	Endothermic	not spontaneous at temperatures in gasification range	
R2	Highly	Endothermic	above	640
R3	Highly	Endothermic	above	620
R4	Highly	Endothermic	above	700
R5	Significantly	Endothermic	above	670
R6	Moderately	Endothermic	above	546
R7	Mildly	Endothermic	above	820
R8	Mildly	Exothermic	all temperatures in gasification range	
R9	Mildly	Exothermic	below	820
R10	Moderately	Exothermic	below	546
R11	Moderately	Exothermic	below	630
R12	Moderately	Exothermic	all temperatures in gasification range	
R13	Significantly	Exothermic	below	670
R14	Significantly	Exothermic	below	700
R15	Highly	Exothermic	below	590
R16	Highly	Exothermic	below	620
R17	Highly	Exothermic	all temperatures in gasification range	
R18	Highly	Exothermic	below	640
R19	Severely	Exothermic	all temperatures in gasification range	
R20	Severely	Exothermic	all temperatures in gasification range	
R21	Severely	Exothermic	all temperatures in gasification range	

2.7 A technical model of gasification

There are many different makes and models of gasifier, as would be expected from a technology that is over 80 years old (Basu, 2013, Chapter 8, "Design of Biomass Gasifiers"; Berkowitz, 1997, Chapter 10, "Conversion"; Higman and van der Burgt, 2003, Chapter 5, "Gasification processes"; Kopyscinski et al., 2010; Liu et al., 2010; Moulijn et al., 2013, Section 5.3, "Coal Gasification").

There are two main kinds of thermally-activated change in the feedstock - thermophysical and thermochemical. Thermophysical changes are those mostly affecting the shape, behaviour and reactivity of the feedstock, rather than its chemical nature. Thermochemical changes are those that involve chemical reactions between individual molecules. There is some cross-over between these two classes of change, however. For example, torrefaction, which is a thermal process, can lead to chemical reactions; and chemical carbonisation reactions can lead to fragmentation and deformation in the feedstock material.

Thermophysical activity enables more surface area of the material to be available, which is (near) where most of the thermochemical reactions between gas molecules and solid molecules will take place. Catalysts will promote these reactions. Most gasification reactors have an area where gas molecules can accumulate, and this is where most of the reactions between gas molecules take place. However, some gas molecule to gas molecule reactions will take place near the surface of the material : as solid molecules become gas molecules from primary reactions, before they can

migrate far away from the material surface, they become available for reactions with other gas molecules produced near the surface of the material.

Many of the reactions that take place at the surface of the feedstock material or very close to it are highly exothermic - that is, they release a lot of heat. Heat exchange from this area to the rest of the reactor is hard to manage, and will skew the overall balance of reactions in the reactor, which is why many feedstocks are pulverised, shredded or chipped before being gasified. It is also why circulating reactor designs are favoured : the feedstock is moved around in the reactor by a variety of means including being driven by input gas, or being "bubbled" by applying intense heat underneath the reactor. This will not only help to avoid "hot spots" in the reactor, but prevent sintering - the coalescing and compacting of unreacted feedstock into solid masses that make it less likely to gasify. Another way to avoid hotspots, unreactive clusters and chemical inconsistencies is by the use of "entrained flow", setting up a reactor where all the products and reactants are kept moving in one direction along a predetermined pathway, such as in pipes or tubes.

At the high temperatures in a gasification reactor, water will invariably be present as steam - a gas. Also, many molecules and compounds in organic feedstock - biological or fossil fuels - will tend to vapourise at the high temperatures in a gasification reactor. Thus, many of the thermochemical reactions will be gas to gas.

The main influence on the overall balance of reactions in a gasifier will be the relatively slow speed of heterogeneous reactions at the surface of the feedstock material - that is, reactions between solid carbon and non-carbon gases (Basu, 2013, Section 7.3.3.1, "Speed of Char Reactions"; Higman and van der Burgt, 2003, Section 3.1.3, "Char Gasification"). Carbon remains in the solid phase until around 4,800 degrees C, and gasifiers operate at much lower temperatures than that, so all carbon produced in gasification reactions will be in the solid phase. This means that there will be solid to gas reactions throughout the reactor, once the carbon molecules have left the body of the feedstock.

Another key influence on the final composition of gas products from a gasifier is that some chemical reactions are endothermic (taking heat in) and some are exothermic (giving heat out). If significant heat is lost to some reactions in one section of the gasifier, this can reduce the overall efficiency of the gasifier. If significant heat is generated in part of the gasifier, this can distort the chemistry of the process and therefore the heating value of the output product gas. The overall performance of the gasifier should be mathematically modelled, and theory checked against operational data, in order to ensure it is working as desired. The reactions of carbon with oxygen provide most of the heat energy to sustain the gasifier working temperature even though some of the other reactions are endothermic (Liu et al., 2010, page 164). Of note : the methanation reactions will increase the heating value of the output gas product (Liu et al., 2010, page 165). Conversely, if the gasifier is set to favour the production of hydrogen and its partner carbon monoxide, the resulting syngas will have a lower heating value, but a higher utility for chemical engineering, such as for the production of synthetic fuels and ammonia.

Where the gasifier feedstock has a high percentage of hydrocarbons or carbohydrates, the chemical reactions will initially produce complex compounds, but repeated re-reactions assisted by the high temperatures will result in a higher proportion of simple gases; and at higher temperatures, all carbohydrates are expected to be consumed, and no hydrocarbon more complex than methane (CH₄) should survive (Liu et al., 2010, page 166).

There are generally some contaminants in gasifier feedstocks that will take part in chemical reactions. Generally, resulting compounds with sulfur and nitrogen compounds are the most important to eradicate, and they tend to compete with both carbon and oxygen molecules in reactions.

2.7.1 Thermophysical

2.7.1.1 Dessication

(approximately 100 degrees Celsius and above)

Water molecules not chemically bound in the material, on or near any surface, or with a route to the surface it can migrate through, will evaporate from the surface.

2.7.1.2 Torrefaction

(approximately 100 degrees Celsius and above)

If the material being heated is biological in origin, in addition to dessication, some of the more complex matrix structures may decompose - shred, crumble or powder - as they give off volatile substances, and in some cases there are chemical reactions, for example Maillard Reactions. Torrefaction makes biomass brittle, which enables milling into fine particles suitable for gasification. If biomass is torrefied before gasification, and it needs to be transported, it is often compacted as well, as torrefaction causes a significant loss in density of the material, and could lead to explosive conditions. The feedstock may then need to be expanded again before being gasified.

2.7.1.3 (De)-volatilisation

(all temperatures above 0 degrees C)

Organic and inorganic compounds not chemically bound in the material, which have a boiling point lower than the temperature of their environment (approximately), and are on the surface, or have a route to the surface, will migrate to and evaporate from the surface.

2.7.1.4 Fragmentation

As water and volatile compounds evaporate from the surfaces in the material, and the material suffers thermal degradation, it can experience disintegration and granulation, breaking up into fragments and particles.

2.7.1.5 Deformation

Depending on the material, micro-scale channels may open up, meaning that porosity can increase, internal crystals, lattices and layers may dislocate, and surfaces become pitted or notched with nano-scale features.

The processes of torrefaction, fragmentation and deformation will collectively increase the surface area of the material and so facilitate thermochemical change via chemical reaction.

2.7.2 Thermochemical

With many gasifier designs, several zones form, at different temperature ranges, where certain kinds of reactions predominate. However, all reactions may occur within all zones - dependent on the molecules in the reaction gaining sufficient heat energy from their environment, or the reactions being promoted by catalyst molecules. Reactions can occur in cascades, as the products of one reaction can become reactants in a further reaction. Several of the reactions are reversible (equilibrium reactions), and the final products are determined not only by temperature and pressure in the reactor, but also by heat distribution within the reactor and the availability of molecules for the reaction. In other words, reactions will essentially compete for reactants, and some reactions may cause bottlenecks, leading to tendencies for some chemical species to dominate in each zone. Also, some reactions happen slower than others - these are known as "rate limiting" reactions, and this is also a factor that determines the segregation into zones.

The chemical reactions may be known by several different names, depending on the context in which they take place, or what they are used to produce. Reactions that produce methane, hydrogen or carbon monoxide are properly known as "gasification reactions"; those that react carbon are "char gasification reactions"; the reaction between carbon and hydrogen is "hydrogasification"; and those that gasify using steam are "steam gasification reactions". Amongst the whole set of possible reactions, those that add hydrogen are "reduction reactions" or "hydrogenation reactions"; those that add oxygen are "oxidation reactions" or "combustion reactions". Reactions that produce methane are "methanation reactions", and reactions that produce carbon are "carbonisation". There are also some special names for certain reactions, such as the "Water Gas Shift Reaction", which originated from the historical production of gas by blowing steam over incandescent carbon coke to produce a gas high in hydrogen ("Water Gas") and carbon monoxide (see Table 9).

2.7.2.1 Pyrolysis Zone

This is anoxic, that is, requiring no additional oxygen other than that from the feedstock.

2.7.2.2 (Partial) Oxidation or Combustion Zone

This is oxidic : requiring (some) oxygen from other zones, or oxygen supplied to the reactor as gas. This is where oxidation/combustion reactions predominate.

2.7.2.3 Gasification Zone

This is where gasification reactions predominate.

2.7.2.4 Reduction or Hydrogenation Zone

This is where reduction reactions predominate.

A selection of the possible reactions are shown (see Table 9). Note that the use of the colon indicates the contact for the reaction. A molecule in the gas phase reacting with a molecule also in the gas phase is : "Gas:Gas" (homogeneous reaction). A molecule in the solid phase reacting with a molecule in the gas phase is : "Solid:Gas" (heterogeneous reaction). The solid to gas reactions are reactions with carbon, which may be part of the feedstock material or be free in the reactor, where it would eventually agglomerate or coalesce with other carbon molecules to form soot, and in many reactor designs, gravity is used in one way or another to separate this from the gas

products. Carbon powder accumulations and any remains of the gasified feedstock are known as char, and are very rich in carbon. In ideal conditions, all the char is gasified.

2.8 The production of manufactured gas

2.8.1 Microbiological and thermochemical methods

The decomposition of once living matter, both plant and animal, in the general absence of oxygen as a gas, under the action of microbiological agents, is widely in use today for the production of biofuels - principally biogas and bioethanol. Although anaerobic digestion and fermentation of biomass are highly efficient energy conversions, and there are plans for increasing deployment, given sufficient feedstock (Messenger, 2014b), it is to be expected that industrial-scale thermochemical and electrochemical treatments of biomass will eventually give an order of magnitude greater production volumes. Nevertheless, in the meantime, in some regions and sectors, anaerobic digestion and fermentation of biomass is not well-developed, but should be, as much carbon value is not yet being captured. The use of biomass in manufacturing gas is going to give far lower net carbon dioxide emissions than the use of coal.

The gasification of coal has a long history, and technologies for thermochemical treatments of coals are consequently well-researched. It would be cautious to project that in the short-term fossil fuel gasification is more likely to integrate successfully into a system designed for Renewable Gas than biomass inputs. The plant could be built today, but the gas produced would be a Transitional Gas (see Table 10) rather than a fully Renewable Gas, until a supply chain and suitable pretreatments for biomass feedstocks were developed and the technology fully optimised for biomass. Since permanent geological sequestration of carbon dioxide is not yet widely practiced, carbon recycling would be the optimal treatment, meaning a Transitional Gas system with fossil fuel inputs should be operated as a centralised, self-contained Power-to-Gas grid backup plant, to maintain low net carbon dioxide emissions to air. Other configurations of Renewable Gas - such as providing low carbon gas pipeline supplies, or feedstocks for synthesising low carbon fuels or other chemicals, need biomass inputs in order to attain low emissions status, as the carbon is not captured or recycled. However Biomass-to-Gas could take some time to perfect and make widely available.

Table 10 : A Terminology of Gas

"Earth Gas"	Gas that is sourced from inside the Earth. It is produced by geological processes at depth, but it may migrate upwards to more shallow locations, where it can be trapped. It is brought to the surface either by geophysical processes, such as vulcanism, Tectonic Plate subduction, mantle upwelling, the development of seeps or chimneys; or by mining. It may or may not contain methane. It may or may not be combustible, and so it may or may not have an energy value. This resource is finite. This term is not used in this text because when translated literally into languages other than English, it is a term reserved to denote Natural Gas.
Natural Gas	Natural Gas is gas that is sourced from deep inside the Earth, that usually has a medium to high methane content, which could be referred to as Natural Methane. It is produced by geological processes at depth, but it may migrate upwards to more shallow locations, where it can be trapped. It is brought to the surface either by geophysical processes, such as vulcanism, Tectonic Plate subduction, mantle upwelling, the development of seeps or chimneys; or by mining. Because it contains methane, this gas is combustible and has an energy value. This resource is finite. In some circumstances, Natural Gas may have high levels of nitrogen or carbon dioxide, which means it has a low energy value. In the case that it has a significant hydrogen sulfide content, this renders it toxic to most lifeforms. Natural Gas

includes thermogenic gas (fossil gas), geogenic gas and possibly some archaeogenic gas, but does not include biogenic gas.

thermogenic gas	The term thermogenic gas is used to describe gas that originates from the action of high temperatures and pressures at depth, and over time, in the Earth's crust, operating on ancient biomass (Etiopie et al., 2013a). Thermogenic gas may be formed at any stage in the deep geological decomposition of organic material (biomass), including gas produced in secondary processes from fossil fuels such as coals or petroleum oil. The term fossil gas is used in preference to the term thermogenic gas in this text to avoid potential confusion.
fossil gas	Fossil gas is a term used to describe gas that originates from the action of high temperatures and pressures at depth, and over time, in the Earth's crust, via geological processes acting on ancient biomass. This term is used in this text in preference to the term thermogenic gas. Fossil gas is usually used in counterpoint to the term Renewable Gas, as fossil gas is finite, whereas Renewable Gas is not.
geogenic gas	The term geogenic gas is used to refer to gas that originates from the action of high temperatures and pressures at depth, and over time, in the Earth's crust, operating on inorganic material, such as volcanic rock. Another term for this could be "abiotic" gas (Etiopie et al., 2013a), or "abiogenic" (Etiopie et al., 2013b; Spulber, 2010). The replacement rate of geogenic gas in the Earth's crust is not sufficient to make it an infinite resource. There is some overlap between thermogenic gas and geogenic gas as life on Earth has existed for billions of years, and some organic material has been converted into rock; and also because thermogenic gas will react chemically with the rocks in its surroundings. Some geogenic gas will come to form a constituent of Natural Gas resources. For example, nitrogen present in magmatic rocks is geogenically introduced into some Natural Gas resources. Natural Gas can contain high levels of carbon dioxide, the levels of which rise with the age of the organic matter from which the gas derives. This means that Natural Carbon Dioxide is most likely to be thermogenic - derived from organic matter. Natural Hydrogen by contrast, is most likely to be purely geogenic - derived from inorganic matter. Some Natural Methane has been found to be geogenic by studying atomic isotopes (Etiopie et al., 2013a).
archaeogenic gas	Archaeogenic gas refers to the gas produced by microbiological action on geogenic gas. Examples include the production of gas by microorganisms of the Archaea phyla, feeding on Natural Hydrogen, hydrogen sulfide and other geogenic plumes, chimneys or seeps, such as can be found at deep sea thermal vents. Some constituents of Natural Gas could theoretically be archaeogenic, if the Natural Gas has migrated to reside in fields, caverns or hydrocarbon pools closer to the Earth's surface, at depths where some microorganisms have still been found to survive, although this is highly unlikely.
biogenic gas	Biogenic gas is a term reserved for gas that originates from recently living biomass that has undergone shallow burial by Earth surface processes, and which is then subject to the same microbiological decomposition as occurs on the Earth's surface. This produces methane that leaches or seeps out to the atmosphere. Another term for this could be "microbial gas" (Etiopie et al., 2013a), but this term is not used in this text because it could cause confusion with archaeogenic gas.
chemogenic gas	Chemogenic gas is produced from the appliance of industrial chemistry. The term "manufactured gas" is used in this text instead of this term in order to avoid possible confusion.
Natural Methane	Natural Methane is gas that is sourced from deep inside the Earth, either from thermogenic or geogenic processes, and is mostly composed of methane. It can migrate to the surface and some places show high concentrations.
Natural Hydrogen	Natural Hydrogen is gas that is sourced from deep inside the Earth, and is mostly composed of hydrogen. It can migrate to the surface and some places show high concentrations.
Natural Carbon Dioxide	Natural Carbon Dioxide is gas that is sourced from deep inside the Earth, and has a high carbon dioxide content. It can migrate to the surface and some places show high concentrations.

Sour Gas	Sour Gas is a Natural Gas that has a high hydrogen sulfide content and usually also a moderate to high carbon dioxide content. The term is sometimes interchanged with the term "Acid Gas".
Acid Gas	Acid Gas is a Natural Gas that has high levels of both hydrogen sulfide and carbon dioxide. The term is sometimes interchanged with the term "Sour Gas".
biomass	Biomass is organic, carbon-rich material sourced from recently living and now deceased plants and animals.
bioenergy	Bioenergy is a group of materials that are derived from biomass and that carry an energy value.
biogas	Biogas is gas that is sourced from the Earth's surface, produced by the action of microbiological organisms, using a feedstock of biomass. It may or may not have an energy value. It usually has a significant level of methane and carbon dioxide.
biomethane	Biomethane is a high-methane gas derived from biogas through concentration, separation, washing, cleaning or chemical conversion of some of the biogas constituents to methane.
biohydrogen	Biohydrogen is a high-hydrogen gas derived from biogas or biomass, thus microbiologically-produced hydrogen. One of the ways it can be made in meaningful quantities is through the dark fermentation of biomass.
syngas	Syngas is a compaction of Synthesis Gas. Syngas is an industrially manufactured product. It is generally used in the synthesis of other chemicals, but it is an energy fuel in its own right, as it is largely composed of hydrogen and carbon monoxide. Syngas is usually produced by the gasification of fossil fuels.
SNG	SNG is a compaction of Synthetic, Synthesised, Simulated, Substitute or Supplemental Natural Gas. SNG is an industrially manufactured product. It usually has a medium to high methane content. It is made to replace the use of Natural Gas in industrial and energy systems. It is a gas derived from syngas, or from similar processes to those that make syngas.
biosyngas	Biosyngas is a syngas that is derived from biomass, biogas or biomethane. Biosyngas is usually produced by the gasification of biomass.
bioSNG	BioSNG is an SNG that is derived from biosyngas, to have an enhanced level of methane.
Low Carbon Gas	Low carbon gas is a term used for gaseous phase energy fuels that have a low-to-zero net carbon dioxide emissions profile. They can be derived from fossil fuels as long as the carbon dioxide that results is captured and permanently geologically sequestered (Carbon Capture and Storage or CCS), or captured and re-utilised (Carbon Capture and (Re)-Utilisation or CCU). If CCU is employed to make new fuel, the use of this fuel must also be subject to carbon capture (either CCS or CCU). Carbon-rich wastes such as landfill waste and plastics can be substituted for fossil fuels in low carbon gas systems.
Transitional Gas	Transitional Gas is a term used to describe low carbon gas produced either by Renewable Gas technologies being used with fossil fuel feedstocks, or gas sources that will eventually expire, such as Nuclear Hydrogen. Transitional Gas is already a low carbon gas, but to become fully Renewable Gas, where possible, the feedstocks need to be transitioned so they are sourced from biomass instead. Examples would include gas derived from coal where the carbon has been sequestered (CCS). In future the same gas production plant would be using biomass feedstocks instead. Another example would be Transitional Methane - produced from the chemical reaction of Renewable Hydrogen with carbon oxides sourced from fossil fuels. The same plant could produce fully Renewable Methane if Renewable Carbon were sourced instead of carbon oxides derived from fossil fuels.

Renewable Gas	Renewable Gas is a term that describes a gas resource that is a low carbon gas, and that is produced from resources that are not finite. Renewable Gas includes such diverse gases as biosyngas, bioSNG and Renewable Hydrogen. Renewable Gas should be fully sustainable, so excludes Transitional Gas. Over time, as the use of fossil fuel resources becomes unviable or restricted, for example due to emissions restrictions, fossil fuel-derived low carbon gas should be abandoned and replaced by Renewable Gas production from biomass or Young Carbon.
Young Carbon	Young Carbon refers to sources of carbon that are young in the geological carbon cycle – for example, muds, silts and recent shallow seabed sediments, that have not yet been subducted into the Earth or subjected to shallow burial. Their use is not strictly carbon-neutral, so they should only be used where they can be certain to be replenished in a short timeframe. Young Carbon would not normally be considered to be biomass, but may have a high enough organic carbon content suitable for some Renewable Gas technologies.
Renewable Hydrogen	Renewable Hydrogen refers to hydrogen produced by a variety of techniques using renewable electricity and renewable feedstocks, such as biomass or Young Carbon.
Nuclear Hydrogen	It is not clear if there will be a significant renaissance in nuclear fission power production. However, the current fleet of nuclear reactors will take several decades to decommission. Many nuclear reactors are ageing, and some nuclear power plants (NPP) are showing increasing unreliability. Should electricity distribution networks consider refusing an NPP transmission entry to the power grids, hydrogen could be produced from the reactor heat and used for power grid load balancing services. Eventually, all nuclear reactors will be decommissioned, although hydrogen can be produced during this process. Nuclear Hydrogen is thus a Transitional Gas.
Renewable Methane	Renewable Methane refers to methane produced from Renewable Hydrogen and Renewable Carbon via the chemical reactions for methanation.
Renewable Carbon	Renewable Carbon refers to carbon and carbon oxides derived from biomass or Young Carbon.
CCS	Carbon Capture and Storage : carbon dioxide from any energy conversion, chemical or industrial process is captured, compressed and permanently geologically sequestered (pumped underground for permanent storage).
CCU	Carbon Capture and (Re)-Utilisation : carbon dioxide from any energy conversion, chemical or industrial process is captured, perhaps compressed, and used to make other fuels and chemicals.
manufactured gas	Manufactured gas is mechanically and industrially produced, and is not a result of naturally occurring geological or microbiological processes. Some Renewable Gas is microbiologically derived, some is manufactured. Other Renewable Gas is partly manufactured and partly microbiologically derived.
biopropane	Propane usually made from a biogas feedstock.
bioammonia	Ammonia made using one or a combination of Renewable Gas feedstocks, such as biogas.
green gas	A term used to refer to cleaner, less carbon dioxide-emitting forms of gas fuel. It is not a very precise term and covers a range of technologies and systems. It is almost a pseudonym for Renewable Gas.
green power	A term used to refer to cleaner, less carbon dioxide-emitting forms of electricity production. It is not a very precise term and covers a range of technologies and systems. It is almost a pseudonym for renewable electricity.

Work to develop the gasification of biomass has been ongoing for many years, with mixed success. Although there are a good number of operational systems in existence, and reputable engineering suppliers, it is likely to be some time before there are technology options that meet all requirements, with healthy rates of return on investment, for more than a limited number of biomass feedstocks.

There are three main reasons why gasification continues to be developed, and new designs and plant built. First of all, high temperature gasification produces syngas (see Table 10), a synthesis gas mostly composed of hydrogen (H₂) and carbon monoxide (CO). This has a high utility in all sorts of chemical process engineering : even though biomass can be chemically complex, gasifying creates simple chemical products of value. Secondly, gas chemistry is more straightforward than working with solids. It is not possible to imagine a motorised vehicle driven by a solid stump of oak, however, compressed methane, perhaps produced from gasifying wood and then post-processing the syngas, would be eminently suitable. Thirdly, gasification can produce fairly uniform gas products from a range of non-uniform feedstocks. Despite the varied chemistry of the input feedstock, gasification produces the same selection of the main energy gases.

Coal gasification for the purpose of Transitional Gas power generation could be on a par, or slightly greater, in terms of conversion efficiency, with the best pulverised coal-fired combustion plant - with environmental benefits. Early modelling studies considering coal gasification suggested that more energy could be provided to final consumers via SNG production than combusting the coal to generate power (Dryden, 1975). Many gasifier designs are remarkably similar, but their peripheral processing and cleaning stages define them. Several gasification process designs for fossil fuels offer the possibility to capture carbon dioxide with a very small energy penalty, and prevent it being emitted to the atmosphere, making it potentially a mitigation solution for climate change.

Whether biomass gasification can become widely used is likely to depend on a number of iterations in technology, but if these can be made to work as well with some forms of biomass as for coal, these could in theory generate carbon-negative power if the carbon dioxide is sequestered - Bioenergy Carbon Capture and Storage (BECCS) (Carbo et al., 2011). With the use of biomass gasification to manufacture Synthetic Natural Gas (SNG), if it is injected into a Natural Gas grid, this could provide very low carbon heat to consumers.

Three disruptive process designs are likely to tip investment decisions towards biomass gasification. The first is to incorporate the chemical energy of Renewable Hydrogen into the final gas product. For example, if Renewable Hydrogen is made using surplus, or excess renewable power, from water by fuel cell electrolysis, its cost could be low. Methanating the products of biomass gasification using this Renewable Hydrogen will add fuel energy to the final gas. The second evolution is to use the oxygen generated during the production of Renewable Hydrogen to assist in more efficient biomass gasification. The third step change, which is possible for electricity generation, is to capture and recycle carbon in a closed loop power plant, repeatedly methanating and combusting the same carbon. This would reduce the carbon-rich fuel inputs to the gas system, thereby reducing the total net carbon dioxide emissions, and even reducing the cost of power, perhaps considerably, if Renewable Hydrogen became low cost. If biomass is gasified to bring carbon into the power system, and the carbon is then recycled, then net carbon dioxide emissions of the plant could be close to zero. This kind of power plant would have a high utility in load-balancing the power grid, combusting its methane stores without creating emissions. It would not generate all the time - only when renewable electricity output is sub-normal, or grid power demand supra-normal.

2.8.2 Electrochemical methods

Although thermochemical energy conversion has been the focus in utilising biomass for industrial gas production, electrochemical methods of energy conversion have the theoretical potential to be more efficient.

Electrochemical devices liberate the chemical energy from fuel by channelling the positively-charged ions and negatively-charged electrons from reactants along different pathways before they combine as product gases, thereby breaking the chemical bonds in a controlled fashion.

Electrochemical energy conversion using fuel cells has a long history, but its development has been gradual and discontinuous. However, it is as yet much better developed for the conversion of fossil fuels, mainly Natural Gas, than it is for biomass. Fuel cell hydrogen electrolysis from water is also available.

Energy systems utilising high temperature electrochemical internally-reforming fuel cells may offer strong efficiency gains over the thermochemical gasification of fossil fuels, but further developments are needed.

2.9 Progress in gasification

2.9.1 The design of fires

Organic material, such as recently living plants or animals (known as biomass), or ancient plants or animals (known as fossil fuels), is rich in chemical compounds containing carbon, oxygen and hydrogen. The combustion, or thermally-promoted oxidation, of organic materials, by oxygen in the air, is a series of reactions that results mainly in the formation of carbon dioxide and water vapour, and a small amount of carbon monoxide gas and carbon-rich residues, known as char. Historically there have been two major designs of fires - aerobic combustion in open hearths or fireplaces; and anaerobic combustion - fires that are covered over to starve the reactants of oxygen, leading to incomplete combustion and charred end products such as charcoal and coke.

The way that a wood- or coal-fed hearth fire or garden bonfire evolves as it burns is a well-recognised bulk combustion process - flames of combusting (de-)volatilised constituents that reach up from the feedstock grow and change, and the feedstock changes colour and texture as its temperature increases as a result of the reactions taking place inside. As the char emerges, pieces can become separated from the compacting feedstock and fly off as hot ash. All the while, volatile gases, including complex hydrocarbons and carbon oxides, rise up out of the fire, and tiny particles of tar and carbon billow out of the bed of the fire, suspended in steam, known as smoke.

The technology to engineer enclosed fire and derive valuable mechanical work began with the development of the steam engine that made use of the heat of combustion. Brick- and later metal-enclosed fires for incomplete, or partial oxidation were developed to produce coke, a fuel used in the production of iron, and later steel. At the same time, almost identical furnaces were being used to produce gas to be used as an energy fuel. Feedstock was frequently added from the top or the side, and allowed to become progressively heated. Even though the feedstock could become mobile in the chamber, a fixed bed of char was still the final outcome, and the main structure of these fires remained unchanged - a bed with changing reaction zones above it - dependent on temperature and chemical composition.

Reaction zones in these stratified furnace designs include torrefaction or drying - where water is evaporated from feedstock; pyrolysis, where hydrogen, light hydrocarbons and other volatiles are chemically separated from the feedstock; combustion or oxidation where carbon reacts with oxygen; and gasification or reduction, where oxygen is removed (or hydrogen is added). If air or other gas is required to maintain the preferred kind of combustion, it is supplied in a variety of ways, such as the adoption of blowing gases through small pipes, or tuyeres, into an almost fully sealed reactor, a mechanism adapted from iron ore blast furnaces.

Gas producers, or gasifiers, that have air or oxygen blown in under the bed and draw the gas produced from the top, are called "updraft", and those where the air or oxygen is blown in above the bed and the produced gas is withdrawn at the bottom are called "downdraft". A "crossdraft" gasifier blows air in one side, and product gas comes out on the other side. If fuel and air are fed into the gasifier at the same point, this is known as "entrained flow".

To get better performance from gasifiers, as for earlier combustion chambers, it is better to use denser, more uniform or more piecemeal fuel - however, this can lead to irregular combustion, and poor temperature control, if air or oxygen cannot reach all parts of the combustion bed, even if it is blown directly into the feedstock. Several solutions to this problem have been developed, including mechanically moving the feedstock with underlying grates, through which ash and char and any molten by-products, known as "slag", are removed by gravity ("moving bed"), permitting better combustion of the rest of the fuel. However, the most successful ways to improve and regulate fuel oxidation and partial oxidation are the "fluidisation" of the feedstock - making it act as if it is a fluid, and the use of indirect gasification.

In a fluidised bed, the feedstock has been pre-processed into small particles, and are made to move under the pressure of blown gas, either imitating the effect of a bubbling soup, when it is known as "bubbling fluidised bed" (BFB), or when the whole mass of particulate feedstock is made to circulate in guiding tubes and shafts, known as "circulating fluidised bed" (CFB).

With indirect gasification, there is a separate combustion chamber that provides the heat, which is exchanged into the gasification furnace, to be used to (de-)volatilise and partially oxidise the feedstock. In general, air or oxygen is available in the combustion unit at appropriate levels to sustain full oxidation, but constrained in the gasification section. Heat exchange between the combustion unit and the gasification unit is sometimes mediated by the combusted fuel itself, or an inert material such as sand which is circulated between the chambers. The use of cyclonic chambers, or cyclones, for separating fuel, inert flux (ash) or char from the gases by the action of gravity in a vortex, is an essential part of such designs.

The differential effect of gravity on compounds of different molecular weight is also used in some designs where particles need to be separated from gas in the "freeboard" area of a gasifier, an area away from the main feedstock bed, where many gas-to-gas reactions take place. Besides the use of gravity separation, temperature differentials between separate units of a gasifier plant may also be vital to assist in the condensation of vapourised tars and unwanted light hydrocarbons out of the product gas. Various non-inert, non-feedstock chemicals may also be mixed in as reactive flux, to remove or reduce the levels of unwanted or complex chemicals from the final gas - a technique also used in metal ore blast furnaces.

Almost since the very beginning of coal carbonisation for the production of gas, superheated steam injection has been used to adjust the temperatures of the partial oxidation furnace, and to modify the chemical composition of the output product gas (Howarth, 1864a, 1864b). The

recycling of carbon dioxide, carbon monoxide and hydrogen into the gasifier from its output stream can be also be used to adjust the temperature in the gasification reactor and also the composition of the final produced gas.

2.9.2 Gasification applied to biomass

Gasification is essentially the application of heat of a high temperature to a carbon-rich substance in order to stimulate thermochemical reactions, liberating gaseous phase products. If this procedure is conducted in an atmosphere of plentiful oxygen, it is known as combustion, and the resulting gas is mostly carbon dioxide and water (as steam), neither of which can be burned, and so cannot be used as a fuel. If instead, heat is applied to carbonaceous matter without access to excess oxygen gas, the reaction products are more likely to be carbon monoxide (carbon dioxide less half its oxygen) and hydrogen (one oxygen atom short of water), both of which are flammable, as they still have the capacity to be oxidised. In addition, simple hydrocarbons are potentially formed, such as methane, which, having no oxygen in it at all, is highly combustible.

Gasification requires high temperatures to be sure that volatile gases are produced. If temperatures are lower than the optimum for a particular feedstock, more complex molecules can form, such as tars and other long chain hydrocarbons, which may be in the vapour phase in the gasification reactor, but condense out to liquids or semi-solids when they cool down - biooils (bio-oils) and biotars (bio-tars) where the feedstock is biomass. This is usually termed pyrolysis, and is a stage that all gasification feedstocks must pass through as they are heated in a thermal reactor. Although biotars and biooils can be useful in their own right, and can certainly provide energy in combustion, they are not as flexible as gas products for use in power generation and chemical engineering. However, these biotars and biooils are energy dense compared to gas, and so are more compact in storage, and more efficient to transport, and can also themselves be gasified at high temperatures to produce useful energy fuels. It was envisaged early on that biomass gasification could be conducted in two stages - pyrolysis biooils made in small plants in a location close to where the biomass is grown, followed by transportation to centralised, large scale plant for gasification (Bridgwater and Peacocke, 2000; Faaij, 2006, Section 2.2.4). The reason for this is that unprocessed biomass is less energy dense than fossil fuels - and very widely dispersed - making collection and transportation of raw biomass inefficient. Research into stabilising biooils is continuing (e. g. Bridgwater, 2012; Elliott, 2013).

Gasification is normally considered to be most efficient at high temperatures. However, the lower the embodied energy value of the input fuel feedstock, the more sense it makes to produce a higher heating value gas in output. The optimum fuel in this respect is normally considered to be methane. In order to increase the amount of methane produced when biomass and lower quality lignite or brown coals are gasified, lower temperatures are required. For this reason, some biomass gasifiers that aim to produce gas higher in methane could be more accurately be described as pyrolysers, or pyrolysing gasifiers. The other option would be to pressurise the reactor, which would produce a tendency to form methane by preference.

As biomass feedstock enters a gasification reactor, it begins to heat up. If there is any residual moisture in it, this begins to evaporate out. Then as its temperature increases, the biomass begins to thermally decompose in the pyrolysis phase, and release volatile products, gases such as carbon dioxide, carbon monoxide and hydrogen; and hydrocarbons that would normally be liquid, here in the vapour phase. Some of the material combusts, which raises the temperature. With these reactor temperatures, light hydrocarbons bond to form heavier hydrocarbons, with the risk of these becoming tars that cannot be further reacted by cracking at the highest temperature in the reactor. As pyrolysis continues, the solid components of biomass feedstock that are not taking part

in chemical reactions become separated from the rest of the gaseous material. This non-reacted material is composed of biochar (bio-char) - high in elemental carbon; and ash - high in minerals, such as potassium, sodium, magnesium and iron. Biochar forms because there is not enough oxygen and heat in the reactor for full oxidation-combustion. As the material becomes hotter still, some of this char takes part in gasification reactions with the gasifying atmosphere. In parallel, some of the lighter hydrocarbons will "crack" to gas, or break down by reaction with gases. There will also be gas with gas reactions.

2.9.3 The specific nature of biomass gasification

Biomass has similarities to coal in gasification, but there are some general differences, which suggest modifications to thermochemical treatments and process stages. In particular, there appears to be no way to completely suppress the production of tars from biomass at optimum gasification temperatures and conditions, and so this needs to be accounted for in engineering process design. The length of time that biomass remains in the gasification reactor, known as the residence time, is a key factor to control; as the longer that pyrolysis reactions are permitted to continue, the more likely they are to produce complex long carbon chain molecules or chars.

Although biomass has somewhat or significantly less heating value than coal per unit of volume, the by-product of pyrolysis, biochar, is more reactive in gasification than coal. Another key difference is in the components of the non-reactive ash, that proportion of the biomass that remains after thermochemical processing. In biomass, ash may arise from the original constituents of the plants or animals from which it derived, or may be foreign matter introduced during sourcing and transportation. Ash resulting from the biomass itself can be high in alkali and alkaline earth metal species (AAEM). Moreover, ash from biomass gasification is more susceptible to melting at lower temperatures than the ash from fossil fuels, and when it does so, it can become chemically active in contact with the gasification reactor vessel and its lining. Ash with lower melting temperatures would presumably in many cases prescribe a lower gasification temperature to prevent ash, or ash and char, agglomeration - which would limit how much of the biomass can be gasified - leading to lower "carbon conversion" (Higman and van der Burgt, 2003, Section 5.5).

Many kinds of potential biomass feedstock have a morphology not suited to efficient gasification in their raw state, so they require compacting, drying, torrefying, pulverising, chipping or shredding first. High fibre content in biomass is a limitation in reducing fuel particle size through mechanical means, and some forms of biomass would tend to combust rather than gasify, as their form and chemistry would lead to higher (localised) reactor temperatures. Both of these are rationales for utilising fluidised beds for gasification reactors. Fluidised beds would tend to lower the highest reactor temperatures, which would increase the proportion of methane in the produced gases; however it could also lead to higher tar production, as a result of the lower temperatures.

Although properly prepared biomass has very similar characteristics to "young" or immature coals in gasification (Higman and van der Burgt, 2003, Figure 3.3; Nanou, 2013, Section 1.2.2) there are some key differences, mostly notably for biomass : a lower melting temperature for the mineral or ash constituents (FAO, 1986, Section 2.4.5; Higman and van der Burgt, 2003, Section 5.5); their often greater propensity to devolatilise or thermally decompose to gas products; and how in general they produce chars more ready to gasify - biochars have a higher gasification reactivity. Greater reactivity in the biochars is linked to the structure of the material, and also to the AAEM content in the non-combustible ash, which can act as a catalyst for gasification or combustion reactions (Asadullah et al., 2010).

Fluidised bed gasifiers operated at lower temperatures are suitable for biomass gasification, however, this leads to slower heating of the prepared fuel particles - hence more tar formation from pyrolysis-type reactions. Despite the potentially longer residence time in the reactor operating a fluidised bed, reactions will be a statistical distribution, so there may be the possibility for unreacted individual particles of char to appear in the exit gas stream. Biotars, biochars and "biosoot" or biocoke are repeatedly found to be issues that need to be dealt with.

Lower rank coals have a similar high gasification reactivity to biomass - so co-firing is appropriate. However, the fossil carbon that becomes incorporated into the product gases would need to be captured on combustion.

2.9.4 Contaminants in biomass gasification

Biogas has a number of contaminants, such as hydrogen sulphide and siloxane chains. Gasification produces fuels with potentially traces of tar, carbon dust, and probably some nitrogen compounds. All of these things could potentially damage gas pipelines or combustion plant, or cause banned emissions.

If Renewable Gas, maybe a mixture from a range of processes, is being used at a centralised power plant, some contaminants can be tolerated. However, if the Renewable Gas is destined for the gas grid, it will need to be cleaned - washed or in other ways fractionated to remove the contaminants not permitted.

2.10 Tars, chars, slags and snags

2.10.1 Problematic issues with gasification

Historically, commercial success and economic productivity in biomass gasification have not been guaranteed. Common problems range from low overall energy conversion efficiencies from the feedstock to the produced gas, through to technical problems with elements of the gas cleaning after a gasification stage. Added to technical difficulties, there is also a large number of patents that still apply from fossil fuel gasification, which will probably limit design decisions, and may have prevented learning from being shared in some cases. Yet it is the technical problems that are probably the most significant limitation to the growth in biomass gasification. Their resolution potentially results in higher product gas costs with the technological options available today, and so without attention, biomass gasification could continue to resemble a two-steps-forward, one-step-backwards development path.

2.10.1.1 Incomplete oxidation of carbon

Carbon conversion significantly less than 100% is likely to be usual, and insurmountable. Some biomass gasification proponents have turned this to their advantage, by demonstrating that biochar is a valuable agricultural product. However, incomplete carbon conversion implies inefficiency with the use of the feedstock, which has economic repercussions.

2.10.1.2 Particle size

It appears to be essential to shred, chip, mill or otherwise pre-process all forms of biomass prior to gasification, owing to its characteristics. Together with biomass drying, this represents a not-insignificant cost in preparation of the feedstock. However, it is only a parallel to the need to pulverise coal for the most efficient combustion reactors.

2.10.1.3 Contact time : residence time

The length of time that a biomass particle is in a zone in a gasifier where it can be reacted is critical. It must not be too long, or it could partly melt, or stick to other particles and become less reactive. It must not be too short, or it will not have the opportunity to be gasified. Fluidised bed reactors have answered this question to a great degree, but there is likely to be much scope for improving biomass gasifiers to ensure the optimum contact time for each type of feedstock and feedstock preparation technique.

2.10.1.4 Ash : Concentration of toxic trace elements, slagging and catalytic effects

The non-combustible residual portion of biomass has different contaminants than the ash from coal. There are likely to be toxicity issues with some of the trace elements and minerals that are in the final ash or slag from a biomass gasifier. Cadmium was identified as a problem early on in biomass energy studies (Nielsen and Houmoller, 2001) and solutions are still being found (for example, Fernandez-Pereira et al., 2011).

Biomass ash has a relatively low melting point, compared with the ash from coal. This means that for a high temperature thermochemical reactor, there has to be some form of management of the ash. In coal gasification, it is possible to use the tendency of the ash to agglomerate and melt to create slagging conditions - where the walls of the reactor are coated in solid formerly-created slag and fresh liquid slag runs down on the top. However this is not possible with biomass without modifications, as the molten ash is far more aggressive. To use this approach in a biomass gasifier, for example, would require the addition of flux, perhaps silica or clay, that could help the ash achieve slagging properties; and in addition the slag would possibly need to be recycled to create the correct cohesion properties (van der Drift et al., 2004). Most current design choices for biomass gasification use fluidised beds and lower temperatures, and aim for the ash to either rest in the lower part of the bed or be recycled with chars, aiding with heat exchange. Ash will need removing from the gasifier, which is why grates are often provided at the bottom end of the reactors.

Alkali salts in biomass ash have been shown to have a catalytic effect in gasification (Kruse and Faquir, 2007), and so it is possible that some simple additives to a biomass gasifier could significantly improve gas output and select for particular gas species.

2.10.1.5 Temperature runaways ("hot spots"), explosions

Localised temperature irregularities in gasifiers can be difficult to resolve (e. g. ExxonMobil, 2003). Also, an imbalance in the suite of chemical reactions taking place may lead to explosive conditions. Most of these kind of problems can be addressed by careful preparation of the feedstock and mobilising the contents of the reactor - "fluidising" the reacting particles and gases can even out conditions.

2.10.1.6 Moisture

The high moisture levels in biomass affect the type of gasification that is optimal, and places an energy burden on pre-treatment. Approaches to this problem include supercritical water gasification, conducted at a high enough temperature to draw the water into the gas chemistry, rather than allowing the water to block it.

2.10.1.7 Soot and coke

As a result of incomplete oxidation of carbon in the initial feedstock, and the difficulty in making sure of a sufficient contact time for each particle to fully react, and the balance of reactions that result in carbon formation, there is likely to be carbon soot in the output gas, or carbon coke forming "cake" in part of the chamber. Cyclone chambers are frequently deployed to separate soot from product gases, and this is reasonably efficient. However, there is the potential for explosive conditions to occur, depending on the operational condition of the cyclone and electrostatic phenomena. An explosion in a cyclone would be more dangerous than in the main gasifier - which could normally contain it.

2.10.1.8 Tar management

Here follow methods being explored to prevent or post-process tar production in the gasification of biomass.

2.10.1.8.1 Downdraft gasifier design

The downdraft gasifier designs appear to be effective at controlling the levels of tars produced in biomass gasification.

2.10.1.8.2 Quench, cool, wash, filter and purge

Tars will condense out of the gases and vapours produced by biomass gasification, as the products are cooled, and a selection of quenches and coolers are used in operational plant. If gasification is followed by a shift, this will also be done at a lower temperature.

There are a variety of ways to filter, wash and purge unwanted chemical products from the gas stream after gasification. Güssing Renewable Energy use RME - Rapeseed Oil Methyl Ester (Canola Oil Methyl Ester) - that they produce at the plant - as washing oil (Higman and van der Burgt, 2003, "The FICFB Process").

The Dutch research organisation ECN use their own proprietary "oil wash" filtering system - "OLGA", and anticipated in their early work that the bulk production of their preferred oil "Oil-C" would be inexpensive (Boerrigter et al., 2005).

2.10.1.8.3 Pyrolyse first

The concept is to use two reactors in train, operating at different temperatures, with the first operating in a pyrolysis regime, and the second in a high temperature gasification regime. In the first reactor, if the residence time is short, biooils (bio-oils) are produced - this is known as "flash" pyrolysis. Otherwise, if the residence time is longer, a mixture of biogases and biochar (biocoke, biocoal) are produced with some biosyngas. The second reactor is gasifying biooils and biochar at high temperatures, which should result in very little tar being produced, as complete gasification of the tars can be encouraged with higher temperatures.

2.10.1.8.4 Very high temperatures

Using much higher temperatures in biomass gasification in the correct design of gasifier will reduce tar formation, but will also shift the carbon-oxide balance towards carbon dioxide rather

than carbon monoxide (Zhang et al., 2010; Zhou et al., 2009) This would not be problematic in the case that the carbon oxides are going to be methanated to produce fuel, but there would be an overall energy penalty from this route. Whether this would compensate for the energy required to clean tars out of biosyngas is not certain.

2.10.1.8.5 Catalytic tar suppression and conversion

Iron and nickel are renowned for reactivity, and so there may be opportunities for their use as tar suppression catalysts for biomass gasification. Naturally occurring minerals are frequently employed in chemical engineering as catalysts, or used as the core ("support") of catalysts. Mirella Virginie and colleagues have used iron on olivine supports to suppress tar formation in biomass gasification (Virginie et al., 2010). The use of olivine is intriguing, as in the Earth's crust, serpentinite is formed from olivine by a series of geochemical reactions, at least one of which produces geogenic hydrogen, or "Natural Hydrogen". The Energy Centre of The Netherlands (ECN) use olivine sand in their research and demonstration biomass gasification facilities.

Tars have been captured by the use of clay in different forms, and even sand, by Reiji Noda and colleagues (Noda et al., 2009).

2.10.1.8.6 Recycling of fuel gas

Yan Cao and colleagues showed that recycling some of the product gas from the gasifier would maintain temperatures high enough to decompose tars, and reduced the overall energy input requirements (Cao et al., 2006).

Interestingly, the use of clay features several times in solutions proposed for biomass gasification issues. Before the advent of zeolite catalysts, clay was used in oil refinery as a cracking catalyst (Noda et al., 2009), so there is a precedent for its use in biomass gasification. Besides the potential uses of sands (or sandstones), muds (or mudstones) or clays (or claystones) for tar reduction or for creating slagging conditions to treat ash issues in biomass gasification, there is a potential further opportunity. Muds and clays can form in areas of high biological deposition, at the estuaries or deltas of rivers, or along tidal coasts, for example. Ancient mudflows are the precursors to some fossil fuels, where there was high biological accumulation, for example in deep sea fans (Daly, 2013). Microbiological activity in muds results in methane emissions - biogenic gas from the shallowest of burials - owing to the high levels of organic matter (OM), deposited in them. Climate change is likely to aggravate runoff in some regions of the world - by increasing rainfall - and increasing the severity of rainfall. Cities and states are likely to need to conduct increased dredging to keep ports and waterways open and for inland flood management. Is it possible that dredging mud could be used in biomass gasification? Naturally, it would not be efficient to dry it before use, but in a supercritical water gasifier, the question can be asked if it could potentially catalyse gasification reactions, control the negative impact of inerts, prevent "tar wash" from fouling the reactor, and even provide some "young" quasi-Renewable Carbon for the chemistry.

2.10.2 Issues with Fuel Cells

The main issues with fuel cells of a range of current designs are : heat management, water management, cell voltage control, membrane electrolyte and catalyst integrity, carbon monoxide or sulphur compound "poisoning", and coking - or excess carbon formation - accumulation of particulate carbon dust arising as a solid product of a gas-to-gas reaction.

Various approaches have been taken for heat and water management. For example, water recycling has been shown to stabilise fuel cells in designs that need to maintain a humidity gradient; and carbon dioxide recycling is also likely to be of some assistance with both controlling temperature and preventing carbon formation. In Molten Carbonate Fuel Cells (MCFC), a carbon dioxide supply to the cells is anyway a pre-requisite for their operational chemistry (Desclaux et al., 2010).

High temperature fuel cells - solid oxide fuel cells (SOFCs), and MCFCs, need to retain their high internal temperatures or they will lose efficiency (Larminie and Dicks, 2003, Chapter 7); and in addition, SOFC solid state electrolytes could suffer thermal shock from significant temperature change at speed (Singhal and Kendall, 2003, Chapter 1); this suggests that variable operation would not be optimal; there would be long lead times when starting up and shutting down, and there would be over-consumption of fuel if an SOFC is made to cycle on and off. However, variation in operation would be needed for power grid load-balancing, and this need has in the past put the use of SOFCs into question.

In solid oxide fuel cells (SOFCs), since they are operated at high temperatures, owing to the thermodynamics of gas reactions, carbon monoxide becomes a fuel rather than a "poison", and nitric oxide (NO) and nitrogen oxide (NO₂) (together : NO_x) emissions are low. Besides converting carbon monoxide to hydrogen via the Water Gas Shift Reaction, SOFCs can be run on almost any carbonaceous or other combustible material, especially hydrocarbons (Singhal and Kendall, 2003, Chapter 1, Section 1.10), of which methane is very favourable, either in the form of Natural Gas, or from sources of biological decomposition or other microbiologically induced chemical reaction (Singhal and Kendall, 2003, Section 12.1).

Sulphur "poisoning" issues in SOFCs as in other fuel cell designs can be resolved by de-sulphurising the fuel before it enters the fuel cell stack, however, biologically-sourced gases could have high levels of sulphur compounds in them, which poses a problem for the cost of pre-treatment.

Because PEMFC operate at a low temperature, they require noble metal catalysts, such as platinum, to function, although new catalyst fabrication means that much less platinum is required than when they were first developed (Larminie and Dicks, 2003, Section 4.3). SOFCs don't need to use noble metal catalysts as they operate at high temperature.

Future developments could possibly lead to lower temperature SOFCs, which would be beneficial regarding materials integrity - even though the designs do not suffer from the kind of corrosion experienced by Molten Carbonate Fuel Cells (MCFCs). A balance would need to be found however, because there are good reasons to keep SOFC temperatures high, which include the conversion of carbon monoxide, and better kinetics at higher temperatures - good gas flow ensures that unused fuel and exhaust products are easily removed from the fuel cell stack, and assists with heat management. SOFCs could also become more flexible - in switching between operating modes, such as between SOFC and solid oxide electrolysis cell (SOEC) mode - to produce hydrogen.

Whilst carbon dioxide is merely a diluent in an SOFC, it can cause the production of carbon monoxide in PEM fuel cells via the Reverse Water Gas Shift Reaction (de Bruijn et al., 2001). Running a PEMFC at a temperature over 100 degrees Celsius could make it less susceptible to carbon monoxide poisoning, and offer better gas transport as none of the water in the stack would be liquid (it would all be steam).

If SOFCs are run as syngas producers, via internal reforming, whether direct or indirect, they will not necessarily need pure oxygen to be provided to the fuel, as any oxidant should be sufficient in the right proportions. This would mean that an Air Separation Unit (ASU) would not be needed and this would significantly reduce the capital costs of the complete set of equipment - fuel cell stack and BoP (Balance of Plant).

Power electronics is improving and is likely to answer most stack and cell voltage drift when using fuel cells in grid applications. Improvements in materials science is answering concerns about solid state electrolyte manufacture (e. g. Basu, 2007; Liu et al., 2013) and carbon formation. Coking can also be addressed by carefully controlled operating conditions, by pre-reforming heavier hydrocarbons in the fuel destined for SOFCs, and in some cases by the use of steam mixed with the fuel.

Stack operational reliability is improving with continued development, but for some designs and components, step changes in performance are still required. This is probably the area in gas technology that has the greatest scope for research and development investment, but also the greatest potential, as fuel cells are theoretically highly efficient in energy conversion.

3. Interesting serendipities

It is of great interest that hydrogen and methane gas have such high energy release on combustion and in chemical conversion in fuel cells. They are very simple molecules, and their anticipated wider use as energy fuels will address both necessary restraints on net greenhouse gas emissions, and local environmental pollution, including air quality issues. Although an internal combustion engine fuelled by hydrogen might still produce nitrogen oxides (NO_x) that need capturing, a hydrogen fuel cell-drive should produce none at all. A compressed biomethane (CBG, directly equivalent to a compressed natural gas or CNG) engine for a vehicle should not need the most high technology catalytic converters on exhaust pipes in order to protect urban health. Being such simple molecules, hydrogen and methane are involved in a variety of chemistry, and so production processes and other reactions, including combustion, could be expected to be efficient and clean.

The putative development of carbon recycling will reduce the amount of carbon dioxide emissions to air from the energy system - a major step. The displacement of Natural Gas by Renewable Methane and biomethane (from biogas) in the gas energy systems will help in the reduction in leaks or fugitive emissions of fossil methane from the energy production and supply systems, the second most significant greenhouse gas after carbon dioxide.

The co-production of hydrogen and methane in decomposition processes such as anaerobic digestion of biomass is serendipitous. The microbial communities that take part in decomposition have evolved over hundreds of millions of years, or even billions, and indicate that both hydrogen and methane have been ubiquitous fuels and waste products right from the dawn of life. It is perhaps therefore not coincidental, and potentially very helpful, that experimental mixtures of hydrogen and methane gas (hythane) show the potential for efficient gas fuel combustion. Because of this chemistry the injection of Renewable Hydrogen or biohydrogen into gas grids is likely to be commonplace in future, as low percentage volumes will not adversely affect end-use appliances. In power generation, it is possible to employ designs of gas engines and gas turbines that can successfully use this fuel mixture. It is possible that hythane fuel could permit faster

startup or ramp up times and greater fuel use efficiency - as hydrogen has a higher flame speed than methane.

The four main molecular species, methane, hydrogen, carbon monoxide and carbon dioxide are generally the most significant products of a variety of Renewable Gas processes, permitting mixing in gas storage, and easier upgrading. The development of high volumes of Renewable Gas will be of great use in the production of alternative liquid transport fuels, as refinery, or "biorefinery", of the main four gases form precursors to the most useful liquid options.

As Renewable Electricity continues to be deployed, its variability means that it needs to be supported by power generation using fossil fuels. This start-stop nature of back up will require all new plant that gets built to be flexible in use. This new investment means there is an opportunity to make sure that new fuels are catered for - new gas turbines should not only be capable of faster start and stop cycles, but also capable of burning a range of fuels, such as grades of Renewable Gas. With the surge in the use of Renewable Electricity, more fuel storage will be needed, as it will not be required constantly, only during peak periods or as backup. With foresight, this new storage will be built fit for Renewable Gas as well.

Carbon dioxide is a common and easily collectible by-product of many industrial chemical and refinery processes, and so carbon recycling is a logical goal. The readiness with which carbon dioxide can be taken up fully or partially to methane with the reactive addition of hydrogen is an opportunity not to be missed.

The development of Renewable Gas at an industrial scale will make use of existing infrastructure, including pipework grids, storage facilities and industrial plant. It will not be necessary to construct parallel infrastructure as it would in order to push forward a purely hydrogen economy. Carbon recycling will avoid heavy investment in additional infrastructure for Carbon Capture and Storage (CCS), methods of permanently sequestering carbon dioxide in geological facilities.

A major development in the production of Renewable Gas could be expected to aid economic stability in the energy sector, as the main oil and gas companies and corporations will have many roles to play in the development and deployment of Renewable Gas, and so investments in these companies will be secured, even as global decarbonisation of the energy sector takes place. Developing greater volumes of Renewable Gas will displace fossil gas and some fossil oil, but fossil fuels will still play a part in the transition to a much lower carbon energy economy. Coal can still play a part, provided it is used in the most efficient way, in high temperature gasification, and the resulting carbon dioxide from the burning of the coal-derived syngas is recycled into Renewable Gas, and toxins such as mercury and lead are kept from the air, perhaps encapsulated in inert vitrified slag.

4. It's all been done before

The great thing about gas fuel is that it's all been done before. The industrialised countries have over a hundred years of producing and supplying gas fuels of various kinds by pipe networks. There is existing infrastructure and safety and operational standards for working with gas fuels. Countries don't need to create an entirely new energy system to begin to use Renewable Gas.

If you travel around cities and towns in the United Kingdom you can still see remnants of specialist gas fuel facilities that were used before Natural Gas became the dominant gas product. Town Gas storage cylinders, often sited by canals or railways, where coal could easily be supplied to, are

engineering relics, and continue to slowly rust away. Town Gas was made from coal, and was mainly composed of hydrogen, carbon monoxide and methane - with traces of other gases. Town Gas was the main gas fuel in both the UK and the USA until the changeover to Natural Gas, whose main component is methane, with a few slightly longer chain hydrocarbons thrown in.

5. A little history of energy futures

Three decades ago, great hopes were pinned on the development of new nuclear power reactor designs - both fission and fusion, and on the potential offered by the production of synthesis gas (syngas) made from coal, to avoid future oil shocks. We were to have Generation III and Generation IV nuclear energy plant that would revolutionise atomic power generation, be safer, cleaner, the salvation of industrial energy. And making syngas using integrated gasification combined cycle (IGCC) plant would create streams of pure carbon dioxide as a by-product, a gas feedstock which could be used to pump into depleting oil fields to force out more petroleum crude, leaving the carbon dioxide permanently underground, out of harm's way : net carbon dioxide emissions to air were already recognised as a climate-altering problem by serious engineers back in the late 1970s and early 1980s. Ways proposed to dispose of carbon dioxide included pumping it to the floor of the oceans where, under pressure from the seawater above, it would become a supercritical fluid and only slowly diffuse back out to the atmosphere once again (Marchetti, 1977). Syngas could be used flexibly, in the making of methane that could be used to substitute for Natural Gas, and in the production of alternative liquid fuels for transportation.

Thirty years later, gas fuels are still flexible, but nuclear power has proved not to be. The development of fast breeder reactors and other designs has been hampered by technology and cost issues. Fusion power is still a dream. In 1986, Chernobyl happened; and in 2011, after a decade of pledges to a nuclear "renaissance", Fukushima Dai-ichi units suffered irreparable breakdown - both major accidents from which the human race is still working at high cost to recover from. There is significantly less appetite for nuclear energy than before, and the banks, credit ratings agencies and insurance firms are reluctant to over-commit on atomic prospects.

Syngas made from coal remains a good option, but the underground sequestration of carbon dioxide has not really matured to the point of broad adoption, so for future direction this choice is questionable, if "unabated" syngas were to be made from coal without CCS or carbon recycling. IGCC plants may have the appellation "capture-ready", but do not signify that permanent capture will be done. SNG - syngas uprated to high-methane gas - has so far involved large chemical plant with many reaction stages, making it quite costly. Adding CCS would make it even more costly. Carbon Capture and Storage is not developing very rapidly anywhere, or for any purpose. Attaching CCS capability to gas-fired power plants, or even biomass-fired power plants (BECS, BECCS) is a proposal made by several players, but their timelines are hazy. CCS is still expensive, and likely to remain so. It could take politically impossible high carbon prices to make CCS-permitted fossil fuel plants cost-competitive with renewable electricity.

Renewable electricity is likely to remain popular, and a good home for investment. Diurnal and seasonal variation in renewable electricity means that over-capacity is likely in the short-term, and making gas for future use from excess renewable electricity seems pragmatic.

Industrial-scale Renewable Gas projects could help the oil and gas industry to transition out of fossil fuels in an orderly fashion, but this projection relies significantly on ramping up Renewable Hydrogen production.

6. A review of Renewable Gas projects

Over the last few decades there have been several high-profile, and many other, biomass pyrolysis and gasification projects, yet there has been scant progress to fully commercial plant in service. Quite a number of biomass gasification projects are still in the pilot or demonstration phase, and there is continual attrition of companies and projects owing to one or other process or economic difficulties. From small community utilities to large projects with major engineering company involvement, as with other renewable energies, it appears likely that biomass gasification and other Renewable Gas methods will need handholding in the early stages, especially for first-of-a-kind (FOAK) implementations, in new territories, and where technologies are being scaled up or down.

Apart from biomass energy projects built by the larger engineering groups, deploying designs previously functional with coal feedstocks, it can be difficult to follow progress, as virtually each new Renewable Gas project has a new design name and process configuration. Each process design is proprietary, and sometimes it can be complex to check operational data, based on publicly available information. There are sometimes commercially-confidential specific process details, which makes it hard to verify claims. Theoretical and actual energy conversion efficiencies can differ quite considerably, and the economic risk of this, coupled with the risk of operational failures, are probably the biggest barriers to investment in demonstration plant. This means that learning in technological advancement is slow.

Despite this, there is an important potential for Renewable Gas to displace Natural Gas, for example, in the capture of methane from agricultural and waste processing facilities. This is indicated by the contribution to national energy from the German biogas programme - where many local scale biomass digesters have been set up (Dhir et al., 2003); although changes in legislation and other factors could scale this production back (EBA, 2014; Crop Site, 2012). Importantly, it will require growth in industrial scale thermochemical gas manufacture for Renewable Gas to become a significant resource (2050 Calculator, n. d.; Enviros, 2008; Ernst & Young, 2009; National Grid, 2009, 2010; NERA, 2009a, 2009b, 2010, 2011; NNFCC, 2009; REA, 2009). These are often referred to as Advanced Conversion Technologies, or ACT (Hargraves, 2014).

6.1 Who is doing what ?

Renewable Gas can be thought of as a suite of technologies and processes that are for the large part not novel, but are beginning to be implemented and deployed with increasing frequency, both in research projects, pilot demonstrations and in commercial engineering. A review of the extant installations carried out in early 2014 showed a wide geographical dispersal, particularly in Europe, so a decision was made to conduct a study tour across the European Union to visit organisations who are engaged in the various aspects of Renewable Gas.

2014 : Visits made :-

EcoPark Energy Centre, Edmonton, London, England : Waste-to-Energy : municipal waste combustion plant, operating high temperature chambers with comprehensive emissions control : The North London Waste Authority is consulting on upgrading this to a Combined Heat and Power facility

Energy Centre of The Netherlands (ECN), Petten, The Netherlands : Biomass Gasification research project with methane as product gas

Güssing, Austria : Biomass-to-Power plant

Güssing, Austria : Biomass Waste-to-Biogas plant

Güssing, Austria : Biomass Gasification plant, with methane as product gas

Thüga Mainova, Frankfurt, Germany : ITM Power : Hydrogen Electrolysis and Gas Grid Injection demonstration

2014 : Visits proposed but not finalised, or projects not yet operational :-

Audi e-gas Project, Wertle, Germany : Power-to-Gas production, with methane as product gas

Alter NRG, Teesside, England : Waste-to-Energy Plasma Gasification project

GoBiGas, Göteborg Energi, Gothenburg, Sweden : Forestry Gasification project, with methane as product gas (under construction at the time of the review, fully operational since 18 or 19 December 2014 (GoBiGas, 2014))

ITM Power, Cowes, Isle of Wight : Hydrogen Refuelling System (HRS) (originally scheduled to open there in late 2014 (ITM Power (2014c))

McPhy Energy, Berlin, Germany : local hydrogen production and storage solution

MicroBEnergy GmbH, Schmack Biogas, Viessmann, Allendorf, Germany : Hydrogen-enhanced Biogas, "Microbial Methanation" demonstration (due to launch Autumn 2014)

React Energy, Enfield, London, England : Biomass Gasification (project in development stages)

Royal Dahlman, Alkmaar, The Netherlands : ECN MILENA design : Biomass Gasification production plant (at Final Investment Decision stage)

Stedin and DNV Kema/GL, Rozenburg, The Netherlands : Power-to-Gas pilot, with methane as product gas (launched Autumn 2014)

2014 : Visits proposed but refused :-

Shell Pernis, Rotterdam, The Netherlands : PER+ Shell Gasification Hydrogen Process production plant (Shell, 2008b)

6.2 Top level strategy

Some of the ongoing projects to develop Renewable Gas are connected to work streams in the International Energy Agency (IEA). Bioenergy is involved in a number of IEA Tasks that have been operational for the period 2010 to 2012, in particular Tasks 33, 34, 37, 39 and 42 :-

Task 29 : Socio-Economic Drivers in Implementing Bioenergy Projects
Task 32 : Biomass Combustion and Co-firing
Task 33 : Thermal Gasification of Biomass
Task 34 : Pyrolysis of Biomass
Task 36 : Integrating Energy Recovery into Solid Waste Management
Task 37 : Energy from Biogas
Task 38 : Greenhouse Gas Balances of Biomass and Bioenergy Systems
Task 39 : Commercialising Liquid Biofuels from Biomass
Task 40 : Sustainable International Bioenergy Trade - Securing Supply and Demand
Task 41 : Project 3 - Joint project with the Advanced Motor Fuels Implementing Agreement
Task 42 : Biorefineries: Co-production of Fuels, Chemicals, Power and Materials from Biomass
Task 43 : Biomass Feedstocks for Energy Markets

The European Commission and European Union Joint Research Centre (JRC) is active in this area, and the EC DG ENER (Directorate Generale on Energy) has a Bioenergy stream. In the United States of America, the National Renewable Energy Laboratory (NREL) is strongly engaged in hydrogen development, and the Department of Energy (DOE) support a range of projects.

The IEA Hydrogen Implementing Agreement is a global project to increase hydrogen production and the uses of hydrogen (IEA, n. d. b).

6.3 Technologies for Renewable Gas projects

The following cases are not considered to be comprehensive, but indicative of the wide range of operational and demonstration technologies and methods.

6.3.1 Biochemical gas production

6.3.1.1 Anaerobic Digestion

Case : Adnams Brewery, Southwold, Suffolk, England

The first anaerobic digestion plant producing biogas suitable for UK gas grid injection, launched in 2010 (Adnams, 2011). The three microbiological reaction chambers consume organic matter such as brewery and food wastes. The scale and complexity of this project is suitable for mid- to large-scale agricultural enterprises where a significant level of comestibles waste is produced by pre-retail activities, and suggests efficiencies where this has already been broken down by microbiological activity before being composted, such as in the processes to make cheese, yogurt or alcoholic beverages.

Case : Öko Energie Strem, Strem Energy Crop Digestion Plant, Güssing, Burgenland, Austria : Biogas Combined Heat and Power (CHP) and District Heating (DH)

Biomass derived completely from plants is digested using bovine rumen cultures, the biogas then being combusted in a GE Jenbacher gas engine (with another gas engine on standby) to produce both heat and power (Combined Heat and Power (CHP)) for the local community via public wire and local district heating grid (District Heating (DH)) (ReNet, n. d.; Study Tour Notes, 2014). Special techniques have been used to control the odours from microbiological attack on the biomass bunkers/silos (ReNet, n. d. b; Study Tour Notes, 2014). The scale of the buildings used for the energy installation are entirely in keeping with other rural and agricultural construction - neither too large or too high.

Case : Wolf Nudeln, Güssing, Burgenland, Austria : Anaerobic Digestion of Factory Wastes

This noodle production plant uses biomass grown on its own land, and chicken litter from its own egg layers, and some additional waste food, to provide heating and power for the plant. In recent years, the owner of the plant decided that he would only use truly waste biomass and not maize corn in the process as he did not want to "burn bread" (Study Tour Notes, 2014). The design of this plant is industrial in scale, partly because it is using more complex animal-derived wastes as feedstock - however, it does not over-dominate the landscape and blends in easily with other agricultural buildings.

6.3.1.2 Advanced Anaerobic Digestion (AAD)

Advanced Anaerobic Digestion (AAD) techniques vary the types of microbiological culture employed, the numbers, sequence, feedstock residence time, temperatures, pressures and other reactor environment conditions of the digestion processing. These variations are used to promote a higher methane product gas and/or a reduction in contaminants. These are useful for example where the feedstock is waterlogged or dissolved, which rules out traditional "dirt pile" composting. In some cases, there is use of specially selected microorganisms, either at lower than normal temperatures (psychrophiles) or higher than normal temperatures (thermophiles or even hyperthermophiles).

Case : Bran Sands AAD, Teesside, England : Wastewater Treatment with Thermal Hydrolysis (TH)

As an example, Bran Sands AAD aims to produce an increased level of gas from wastewater for use as fuel in a Combined Heat and Power (CHP) facility supplying the sewage plant (Neave, 2009). It is making use of a thermal pre-treatment.

Case : Thames Water : Thermal Hydrolysis Process (THP)

Thames Water are also using a hydrolysis pre-treatment for its sewage sludge to increase biogas output (Thames Water, 2013).

Technique : Upflow Anaerobic Sludge Blanket (UASB) Digestion

There are many examples of plants that use an Upflow Anaerobic Sludge Blanket (UASB) system, whether for sewage (Veolia, n. d.), food (Biothane, 2013) or other organic (Biothane, 2011) processing sludge treatments. Developments in this area appear to be continual. For example, since 2012, Veolia Water Solutions & Technologies (VWS) has made use of Biothane's Biobed Advanced UASB system in its commissioned wastewater plants.

6.3.1.3 Hydrogen production through dark fermentation

Choosing conditions to avoid the production of methane in a bioreactor will result in a higher biohydrogen output. A range of research and pilot projects exist in this space (e. g. Romão et al. 2014), and there are suggestions that combined methods could even increase methane production and/or hydrogen production, depending on the desired product gas (Liu, 2008).

6.3.1.4 Hydrogen-assisted microbiological methanation

Case : MicrobEnergy, Schmack Biogas, Viessmann Group

By careful addition of Renewable Hydrogen to anaerobic digestion reactors, the output methane can be increased. MicrobEnergy is planning to open a demonstration plant in Allendorf, Germany with an initial production volume of 15 Nm³ per hour, increasing to 50 Nm³ per hour (Telephone Interview Notes, 2014, Ulrich Schmack, MD of MicrobEnergy GmbH).

6.3.1.5 Hydrogen-enriched biogas

Case : BioHyGas, Low Carbon Research Institute (LCRI), Wales

Other methods being used to increase the levels of gas energy produced by bioreactors, through the application of hydrogen, includes the trademarked BioHyGas, being researched by the Low Carbon Research Institute (LCRI) in Wales.

6.3.1.6 Landfill Gas, Sewage Gas and other biogas sources

Although there is currently scope for expanding methane collection from landfill sites and sewage treatment plants, the landfill gas contribution to biogas in particular is expected to reduce in volume over time as waste reduction strategies are implemented (Barlaz and dela Cruz, 2010; NREAP UK 2010).

Animal and human wastes will continue to require hygienic disposal, and as time goes by, it is possible these will tend to be thermochemically treated rather than anaerobically digested.

Although in the medium-term biogas feedstocks could diminish, in the short-term, there is much that could be developed but has not yet been.

6.3.2 Gasification

There are several dozen gasification process designs either in production or being actively used for technology demonstration around the world. There are advantages and disadvantages with each design, and the exact process used depends on the input feedstocks and the desired outputs. There have been significant project failures in the last decade or so in the development of these technologies, but there are several factors that will determine future success.

There are several broad categories of development. As the world becomes more serious about carbon emissions control, it is likely that much more investment will be placed into Carbon Capture and Storage (CCS) plants - some of which are essentially gasification units with high purity carbon dioxide output being directed to underground storage for permanent sequestration. Applying CCS could in theory minimise the emissions from the use of coal fuel in straight combustion for power generation sufficiently to permit this practice to continue. Another way to reduce the global warming emissions load from coal burning would be to co-fire or co-gasify coal with biomass - essentially displacing fossil fuel carbon with recently cycled living carbon - and so meaning less disturbance of the global carbon cycle caused by mining fossil fuels. However, instead of combusting coal with or without biomass, and then capturing the waste carbon dioxide for storage, it could well be more efficient to adopt gasification techniques, which would permit the capture of carbon dioxide from the processing in a concentrated form. Gasification has several strings to its

bow – it can also assist with providing alternative liquid fuels to petroleum-based products - as syngas is an ideal starting point for a range of chemistry.

Other environmental concerns are addressed by a whole range of "waste to energy" (W2E) or "energy from waste" (EfW) gasification plant, which would be used for a range of feedstocks that cannot be processed via (Advanced) Anaerobic Digestion or vanilla combustion. These approaches offer the possibility of "zero waste", meeting various regulations about curtailing landfill. Local Authority high temperature waste incineration plants are on a technology continuum with gasification facilities, as they frequently operate at similar combustion reaction temperatures, and may even have oxygen constrained in their operation. Advances in emissions reductions at waste combustion plants (e. g. London Waste, 2014) have paved the way to possible gas treatment designs for gasification facilities.

There has been much experimental research into using 100% biomass in gasification units, and it has been found that the more uniform in composition the input bioenergy feedstock, the better the results. Hence, most gasification plants operate using just one kind of biomass input, such as wood chips. In addition, there are gasification projects that are placing heavy focus on the use of hydrogen, either as an input or an output.

6.3.2.1 Carbon Capture and Storage (CCS) - "Clean Coal"

Although as a fossil fuel it has a progressively limited resource, meaning that the long-term availability of coal for meeting energy needs is not assured, there are ways to use coal to generate electricity that result in less carbon dioxide emissions and toxic environmental pollution than conventional power generation. In addition, these methods could be more efficient than those which use combustion and vent the flue gases and particulate products to air.

Case : White Rose Carbon Capture and Storage (CCS) Project

The White Rose CCS Project is an oxyfuel demonstration project that is to receive UK Government (ZeroCO2.no, n. d.) and European Union (White Rose CCS, 2014) support. The coal-fired power company Drax, engineering company Alstom and cryogenic gas company BOC are in the project team for the power station. The coal will be fired under an atmosphere of pure oxygen rather than air, and some of the carbon dioxide output from the combustion reactor will be recycled, helping to control the temperatures in the reactor and also ensuring that the final flue gas is mostly carbon dioxide and steam, which will be facile to separate, compress and pipe offshore. However, the carbon dioxide capture part of the design is expected to consume more than a fifth of the total output electricity (Global CCS Institute, 2012, Page 8; White Rose CCS, n. d.). In the project's favour, however, it will have the potential to co-fire biomass (White Rose CCS, n. d. b), which should partly mitigate the fossil carbon dioxide emissions from the plant (10%). The UK Government decision to support an oxyfuel project is almost certainly a result of previous pilot plants built by Doosan Babcock (Doosan Babcock, 2013).

Case : NET Power

The Allam cycle is being developed by NET Power as an alternative oxyfuel design, using carbon dioxide as a working fluid - cycling it back to the combustor (Allam, 2013).

6.3.2.2 Co-firing coal with biomass

Case : Drax

Another way to lower the carbon emissions of coal-burning is to co-fire, or mix in biomass with coal in combustion plants (Drax, 2014).

6.3.2.3 Co-gasification of biomass with other fuels

Case : Schwarze Pumpe

The British Gas Lurgi (BGL) gasifier used in the Schwarze Pumpe plant in Germany mixed biomass in with coal in a gasification process (Envirotherm, 2003). Objections to land-based underground carbon dioxide storage curtailed the CCS part of this project (Slavin and Jha, 2009).

6.3.2.4 Coal gasification

Case : Great Plains Synfuels Plant

The oldest established coal gasification plant is Great Plains in the USA. Its product gas is SNG - Synthetic Natural Gas (NETL, n. d. a). Its waste carbon dioxide is exported across the Canadian border where it is used for Enhanced Oil Recovery at the Weyburn field operated by Cenovus, whilst simultaneously effecting Carbon Capture and Storage (CCS) (Cenovus, 2014b).

6.3.2.5 Waste disposal : Waste to energy (W2E), energy from waste (EfW)

There is a growing recognition that systems for dealing with waste streams need to advance beyond burial (landfill) and incineration - both of which cause dangerous pollution of air, water and soils. Besides conventional gasification, very high temperature plasma gasification (plasma arc gasification) is being explored as a means to effectively and safely dispose of a wide variety of waste, including municipal solid waste (MSW), refuse derived fuel (RDF) and commercial and industrial waste (CIW).

Case : Alter NRG, Air Products, Teesside, England

Phase 1 and 2 (Tees Valley 1 and 2, TV1 and TV2) are a collaboration between Alter NRG and Air Products on Teesside in England, using Westinghouse plasma-assisted gasification technology to convert waste originally destined for landfill to energy. When TV1 is in commercial operation, planned for 2015, it will be the "World's Largest Plasma Gasifier" facility (Messenger, 2014a; NRG Focus, 2013).

Case : Advanced Plasma Power (APP), National Grid, Swindon

The UK part of National Grid is running a plasma gasification demonstration in Swindon, England, using Advanced Plasma Power's registered Gasplasma technology (National Grid, 2013).

The efficiency of plasma gasification may result in the mining of old landfill sites after they have stopped producing useful quantities of methane - which is currently captured as "landfill gas".

There is a limit to the use of waste for energy plant as, in the future, the global economy will necessarily de-materialise as a result of climate change policy and declining energy use. The

lower the amount of raw resources pulled into the economic production system, and the lower the quantity of produced goods and packaging that are in the globalised trade markets, the less waste will be produced overall.

Furthermore, it can be reasonably argued that although gasification is efficient and can result in low emissions, the use of biomass for any energy application is inefficient without making use of the resulting heat. Many biomass gasification schemes could theoretically supply local industrial, administrative or residential district heating networks, and yet this is not considered in many project designs in the United Kingdom. A far more integrated approach to utilising combustion and gasification reaction heat is found in other countries in the European Union.

6.3.2.6 Biomass gasification, wood gas, grass gas

The chemistry of gasification is optimal when the feedstocks are uniform. Many gasifiers need to have regular-sized pieces of biomass as input, and a regulated moisture content. For this reason, gasification is often thought of as a technology for making use of the fossil fuel coal - which can be ground and pulverised into powder or compressed into uniform quality briquettes. However, coal supplies are not as uniform as they used to be, or of high quality in many cases. Coal is not a sustainable fuel, neither in terms of its long-term production, nor its environmental impacts.

The management of forestry produces high volumes of tree waste that has a generally uniform quality, and so there are many wood gasification projects in operation. In Scandinavian countries, Austria, Russia and Canada and other countries with copious boreal forests, there are opportunities to strongly develop wood gasification to offset Natural Gas grid use.

Another biomass source that is regular and can be grown just about anywhere is grass. Although most Renewable Gas projects that use grass will treat it with Anaerobic Digestion or fermentation, the possibilities for gasification - either using grass on its own or co-firing with other fuels - are also being explored (Bord Gais, 2010; Judex, 2010).

Studies into available biomass for energy show significant quantities available from annual net primary production (Billion-Ton Update, 2011; Defra, 2013; Slade et al., 2010), more so if there are dedicated energy crop and tree planting programmes (E4Tech, 2009); however harvesting these, especially for centralised energy facilities, may pose problems in areas such as storage and transportation. It would seem best to deliver bioenergy in ways that permit highly localised energy conversion, at the time that the biomass becomes available. Making gas would answer these criteria, which could be used as gas for electricity and heat production, although it is expected that much biomass-derived gas will be directed to the production of liquid vehicle fuels (World Bank, 2010).

It is important to note that as with waste resources (EU, 2011), it is anticipated that biomass resources available for energy in any market could potentially decline over time (e. g. DECC, 2012a, Figure 1) due to competition for the same resources, climate change, land use change and the implementation of a range of legislation.

Case : ÖkoEnergiewelt, Biomasse-Kraftwerk, Güssing, Burgenland, Austria

Despite having faced insolvency in July 2013, this wood gasification facility is still operating (DiePresse.com, 2013; Kurier, 2013), although it is not currently running the Fischer-Tropsch biorefinery unit that formally manufactured biofuels (Study Tour Notes, 2014). Wood is chipped at the facility, and also seasoned, stored on the surrounding land.

6.4 Hydrogen as input or output (or both)

A way to improve the production of Renewable Gas from a gasification plant is to add in value by the use of Renewable Hydrogen as an input to the processing. Waste water, sea water or river water can be separated into hydrogen gas and oxygen gas by the use of electrolysis. This resource of Renewable Hydrogen is named by some as "Wind Gas" or "windgas", or quite commonly "Power to Gas". This can be powered by wind generation when electricity demand is low but winds are strong, and both the hydrogen and oxygen gas can be stored for later use. In a gasification plant, the oxygen can be used to increase the effectiveness of the overall processing in different ways. The hydrogen can be used to increase the value of the output gas fuels - either through mixing or chemical reaction.

The goal of some gasification projects is to make hydrogen gas their main output fuel. They use high temperature gasification to produce syngas and then separate the hydrogen from the carbon monoxide, or shift the carbon monoxide chemically to more hydrogen (and carbon dioxide) by chemical reaction with steam. Most gasification projects burn their output fuel in some way, using turbine generators to produce electricity. Some projects aim to move away from using their output fuel in combustion and instead use fuel cells to generate power - and hydrogen is an ideal gas feedstock for fuel cells. Advances in fuel cells are pointing the way to cost-reduction and less use of expensive rare metals.

Renewable Methane and bioSNG will be valuable gas fuels. In the mid-term, as renewable electricity is deployed at a massive scale, industrial volumes of "Wind Gas" Renewable Hydrogen can become available from electrolysis. Gasification could be a small contributor to Renewable Methane to begin with, but as gas storage begins to take on premium electricity grid balancing value, gasification should become economically enabled. The usual route to Renewable Methane production could then be as a result of Carbon Capture and Utilisation (CCU) - the recycling of carbon-rich waste or flue gases from centralised combustion via reaction with Renewable Hydrogen. If the centralised stores of carbon-rich gas become depleted, then gasification will top them up.

In the longer term, carbon dioxide that has been stored underground as part of Carbon Capture and Storage (CCS) projects can be re-used by reaction with Renewable Hydrogen to create usable methane-rich fuel. This would create a much larger production volume of Renewable Gas than Renewable Hydrogen on its own. Underground Renewable Methane, or Renewable Hydrogen stores, are also a distinct option, as parts of the power generation balancing services move over to the carbon-free economy by combusting hydrogen.

Case : Thüga Mainova, Frankfurt-am-Main

This is a demonstration plant, housed in a shipping container-sized unit on an industrial estate that formerly produced coal gas (Study Tour Notes, 2014). It produces 60 Nm³ per hour of hydrogen from local tap water after osmosis purification. The hydrogen is injected into the Natural Gas grid through a mixing unit, as there is a suitable transmission spur in the area with gas flows of the order of 3,600 Nm³ per hour. As standards pertain at present, amounts above 2% by volume of hydrogen in the gas flow are not permitted, especially if mixing with hydrogen is "upstream" from a Compressed Natural Gas (CNG) station; so if the Natural Gas flow drops below an agreed threshold, the hydrogen plant is shut down. There is almost nothing in the way of gas emissions

into the environment, and little in the way of noise contamination from the plant as it sounds like the deflation of a faraway hovercraft when the plant is being shut down for visits and inspections. The hydrogen plant was provided by ITM Power, and uses proton exchange membrane (PEM) fuel cell electrolyser technology, with a plastic membrane of their own choice, and not the industry standard Nafion. The research data indicates flexibility and reliability of the equipment. Thüga Group is a significant player amongst Germany's utility companies, and this demonstration plant allows them to learn and prepare for Germany-wide grid Renewable Hydrogen and Renewable Methane development, otherwise called the "Gas Battery". The Germany Energy Agency dena have a Power-to-Gas Strategy, and are preparing for somewhere in the order of 10% of Germany's gas to be Renewable within several decades. Some small percentage of that will be Hydrogen, and the remainder, Renewable Methane, produced by methanation. Power-to-Methane demonstration projects are anticipated in the short-term. The Germany Federal Government is supporting this project and others across the country (dena, 2014a) up to a limited volume and for a limited time period. Legislative changes are required to improve the economics of Renewable Gas in Germany, as, amongst other things, end-user taxes for electricity are currently still demanded, even though renewable fuels are being made (Speicher-bar, n. d.; dena 2014b). Organisations are working for hydrogen and methane produced by Power-to-Gas methods to be considered renewable fuels and so exempt from the "Federal Emission Control Act" (BImSchG, 2001).

6.5 Other Chemistry

6.5.1 Advances in the evolution of hydrogen

If the "protonation" of hydrogen ions can be effected at close to room temperature and sea level atmospheric pressure via the use of unusual, low-cost electrodes and a low level of electrical power, or with affordable and sustainable catalysts, then the electrolysis, or photocatalysis (in the presence of sunlight) of hydrogen could become much less costly than via current electrolysers. Even something as basic as the increase in speed of hydrogen evolution could potentially drive down the price of electrolysis (PhysOrg, 2014).

Recent advances in chemistry indicate that hydrogen gas could be more cost-effective to produce from water and other weak acid sources than previously imagined (e. g. De Silva Munoz et al., 2010).

Cheap catalysts for the hydrogen evolution reaction (HER) may come about from nanoscale tinkering (e. g. Kibsgaard et al., 2014).

Supercritical water gasification at high pressure may be able to produce hydrogen in significant amounts from wet biomass, making use of the catalytic effects of salts (Kruse and Faquir, 2007).

Isothermal redox may offer an efficient way to make "solar hydrogen" (Muhich et al., 2013).

6.5.2 Advances in the production of methane

Work is being done to improve the reaction sites on methanation catalysts either through using nanoscale texturing or using unusual substrates for metallic catalysts, or unusual catalysts on metallic substrates (e. g. Zhen et al., 2014).

Work is continuing on heat integration for largescale gasification and methanation plant designs (e. g. Heyne, 2010).

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