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Thermal Processing of Waste

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Dedicated to:

Professor N.N. Greenwood FRS

Contents

Preface

This is the fourth in the series of volumes I have prepared for Ventus Publishing. There are a number of factors which have contributed to my decision to develop the series. One is that, as I said in the postscript to one of the earlier volumes, I am at a career stage where my time is possibly best spent setting out knowledge and ideas I have built up over the decades for the benefit of younger readers. BookBoon provides a splendid medium for this. That is why I very much hope that this fourth in the series will be by no means the last even though I can appreciate the advisability of letting at least a few months elapse before I start work on the fifth. Another reason for my having contributed to BookBoon's range of titles is that the idea of having quality texts financed by advertisements and accessible at no charge is a very good one deserving support. A former colleague in Australia to whom I sent a copy of one of the earlier ones made this very comment. Yet another reason has been anticipated in the previous sentence: I have been able to send the book to friends and colleagues and have been encouraged by the warmth of their responses. Finally, I have derived pleasure and satisfaction from the writing of these volumes.

Let it be noted that by the time I wrote my first book for Ventus I had written a good number of conventional books, the first of which was published as long ago as 1993. This continues, and at the time of writing this preface I do in fact have a conventional book in press. I do not know whether the conventional book will ever be totally replaced by the electronic book, nor do I see that as being relevant to this preface. What is relevant is that I as a writer am getting the best of both worlds.

This book then is concerned with thermal processing of wastes. I first taught this topic at UNSW in 1987. The topic itself, like anything else, has changed with the passage of nearly a quarter of a century and in this book I have needed to set material which I might have taught in 1987 in the quite different circumstances of 2010. Over that period the price of oil has displayed unprecedented fluctuations and greenhouse gas emissions have increased in importance to a degree where it could justifiably be said that they dominate the world political agenda. Fuels originating as wastes do in the modern world have a role which can be related to either or both of these factors and I hope that someone having studied this book will understand why.

Finally, a word about the choice of the dedicatee of this book. Professor Norman Greenwood began at the University of Leeds in the dual role of incumbent of the Chair of Inorganic and Structural Chemistry and Chairman of the School of Chemistry on the same day that I started there as a chemistry undergraduate. His initial lecture to us first year students contained some biographical information, including the fact that his academic career had begun at the University of Melbourne. He was in fact born in Melbourne in 1925 and lived there until he came to Cambridge, England to start a PhD in 1948, thereafter making his career in the UK. I myself lived in Melbourne for a period and when I returned to the UK in 1995 after a very long time spent in Australia (about a quarter of it in Melbourne) I was able to renew my acquaintance with Professor Greenwood. Since then we have exchanged e-mails about our respective experiences of Melbourne which are, of course, very widely spaced in time. This has been a source of considerable enjoyment to me. In 2009 I returned to Melbourne as a Visiting Scholar at Trinity College, where Professor Greenwood had been a Resident Tutor and Lecturer in Chemistry from 1946 to 1948. I began the lecture I gave there with a mention of Professor Greenwood and my association with him. I am pleased and proud to dedicate this book to him.

J.C. Jones
Aberdeen, June 2010.

1. Municipal solid waste

Part I: Nature and amounts

1.1 Introduction

Municipal solid waste (MSW) is composed of household waste and trade and commercial waste and is so called because in ‘developed’ countries it is the responsibility of the municipality in which it is generated to remove it and dispose of it. Amounts of such waste are huge, and quantities in selected places are given in the table below. Comments follow the table.

Place	Amount of MSW	Reference
London, Ontario.	267000 tonnes in 2006	[1]
Kumasi, Ghana.	365000 tonnes in 2006	[1]
China	180 million tonnes expected for 2010	[2]
UK	34.8 million tonnes in 2007/2008	[3]
USA	190 million tonnes in 2009	[4]
Australia	43.8 million tonnes in 2006/7	[5]
South West England	522 kg per resident in 2001	[6]

Reference [1], from which the information in the first two rows of the table is taken, is a comparison of MSW production and management in two cities of widely differing ‘standards of living’: London ON and Kumasi Ghana, respective populations 0.35 millions and 1.61 millions. This gives a *per capita* daily production of 2.1 kg for London ON and 0.62 kg for Kumasi. The difference of a factor of three in amounts is accompanied by a difference in composition for MSW between London ON and Kumasi [1]. There is very much more paper in the London ON waste and more by way of waste from fruit and vegetables in the Kumasi waste. In London ON people often buy fruit and vegetables already peeled and processed. Such processing will not take place locally, London ON having no significant food industry. The waste will therefore go into the industrial or commercial waste stream at whatever places they are produced. In Kumasi by contrast fruit and vegetables will be purchased ‘straight from the land’ and the inedible parts will go into the domestic waste. On the other hand, the processed products in London ON will come in paper wrappings which find their way into the domestic waste stream there.

The third row gives the figure for the whole of China, population 1.4 billion; it translates to a *per capita* figure of 0.35 kg per day. That for the UK, population 61 millions, is in the next row, and this converts to a *per capita* figure of 1.6 kg per day. The trend observed above in comparison of cities – a higher *per capita* amount for the developed community – is shown for whole countries by this comparison of the UK with China. The figure in the next row is for the USA, the world's largest producer of MSW by a fairly narrow margin over China. The *per capita* figure for the USA (population 315 millions) is 1.65 kg per day, remarkably close to that for the UK. The next row contains information for Australia, population 22.2 millions.

A point touched on earlier which will be developed later in the book is that variations in amounts and composition of MSW vary between places and cultures. Nevertheless, wherever people dwell and in whatever way MSW, or its equivalent in places not having a municipal structure, will be produced. The estimated population of the world in 2010 is 6.7 billion. On the basis of about 1 kg per person per day of MSW this becomes about ≈ 7 million tonne per day. MSW as formed has a low bulk density, perhaps 100 kg m^{-3}, whereupon this figure becomes 70 million cubic metres per day.

Anticipating the next chapter on combustion of such waste and also the following section of this chapter in which calorific values will be discussed, the present author has shown previously [7] that a barrel of oil and a tonne of MSW release about the same amount of heat when burnt, approximately 7GJ. World consumption of oil is 80 million barrels per day. Not quite all of this goes into 'combustion' as some is diverted to petrochemical manufacture. Something like a tenth of the daily oil usage could according to this reasoning be replaced by MSW. In fact this simple calculation, though it gives an interesting perspective, does not extend to reality. There are many reasons why MSW is not equivalent in other ways to oil and, as the author put it in a recent talk (subsequently published as [8]), nobody *compos mentis* would offer for a tonne of solid waste the price of a barrel of oil. Indeed, MSW might well have a negative financial value, that is, it might incur disposal charges. Even so MSW has over the decades found fuel use and there is much R&D into this at the present time. A factor in MSW handling by any means is composition variability and this will be discussed in the next section.

1.2 Composition

A study of the composition of MSW from a number of Asian countries [9] and comparison with the waste from the USA revealed the following trends. MSW in India and China had a higher content of putrescible food waste than MSW in the US, respectively 36, 46 and 26%. This is of course the component of MSW which attracts microbial infection with accompanying hazards to community health. The MSW from China and India was found to be remarkably low in paper and cardboard, 5% and 3% in contrast with 41% for the USA and 37% for Japan. The proteins and fats in the food waste are of course combustible and contribute to the heat release in burning of the waste (although high moisture might make for delayed ignition) as are paper and cardboard. Paper and cardboard being cellulosic products have good calorific values (≈ 17 MJ kg^{-1}) and are perhaps the most desirable constituent if burning of MSW is aimed for. There is also a marked difference in plastics contents between MSW from the countries considered in [9]: Japan 15%, Taiwan 21%, China 1%, India negligible and the USA 6%. Plastics are also helpful in eventual combustion. Some have calorific values of around 40 MJ kg^{-1}, approaching the values for petroleum products. There is however one difficulty: the burning of PVC results in formation of dioxin, the most harmful substance to humans known. Atmospheric levels of pg m^{-3} apply, and sudden release of a quantity of 1 kg is a major incident. Monitoring for dioxin in post-combustion gases is possible, and is required when PVC waste is being destroyed by burning. There will also be some textile waste in MSW to the extent of up to about 4% and some wood (e.g., from tooth picks). There will also of course be glass and metals in MSW, perhaps between 5 and 10%. These might have some value, but their importance to the topic of thermal treatment of wastes is that they neither burn nor pyrolyse.

1.3 Calorific values

This was touched on in the previous section, where a comparison with crude oil was made, and will be more quantitatively examined in this section. It was because of the variability of composition of MSW even from a particular place that an investigation into the calorific value of MSW from the USA [10] used simulated MSW, made from controlled amounts of well characterised components blended in such proportions as to represent MSW of typical composition. The composition of the simulated waste in [10] is summarised the in shaded area below.

Newsprint, representing the paper/cardboard in MSW: 35%

Hardwood mulch, representing the wood in MSW: 17%

Polyethylene, representing the plastic in MSW: 14%

Animal feed, representing food waste in MSW: 5%

Silica, representing glass in MSW: 1%

Iron, representing metals in MSW: 8%

Water, representing moisture in MSW: 20%

It ought to be easy enough to estimate the calorific value (CV) of this to within 10% or so. This is in the boxed area below.

$$CV = \{[(0.35 + 0.17) \times 19] + (0.14 \times 45) + (0.05 \times 30)\}\ \mathrm{MJ\ kg^{-1}} = 17.7\ \mathrm{MJ\ kg^{-1}}$$

and the value measured in [10] by calorimetry is 19.2 MJ kg^{-1}

In [10] this is compared with values recorded at a MSW facility in Delaware, which range from 8.4 to 17.6 MJ kg^{-1} with an average of 11.3 MJ kg^{-1}. The value for the simulated waste [10] just exceeds the upper limit of that range, and the reason is that the water content of 20% is low. Whilst MSW can be as low in water as that about 50% would be more typical and 70% not impossible.

In the table below some more literature values are given. Comments follow the table.

Origin of the MSW	**Water content %**	**Calorific value/MJ kg^{-1}**	**Reference**
Changzhou, China	48.5	3.0	[11]
Guangzhou, China	50.1	4.4	[11]
Kuala Lumpur, Malaysia	55.0	In the range 10.0 to 16.8	[11]
Parona, Italy	20 to 30	In the range 10.5 to 16.7	[11]
Paris	35	8.4	[13]
Tehran	65	5.0	[14]

The high value for KL is due to large amounts of putrescible food waste (51.9%)[1] and plastics (21.0%). A reader should compare these with the values for the respective constituents given in the shaded area above. A similar value for KL from a totally independent investigation is given in [12]. Reference [14], which long predates any of the other references in the table, also gives figures for a number of South East Asian cities. For example, the figure for Hong Kong at 60% moisture is given as 9.3 MJ kg^{-1} which is broadly consistent with the much more recent figure in the table for KL.

When the calorific value of a fuel is determined in a bomb calorimeter the value obtained is the higher heating value (HHV). This is the value on the basis that all of the product water condenses and in so doing contributes the heat effect of the phase change to the calorific value. This is in contrast to the lower heating value (LHV), which is the heat obtained if the water in the products remains in the vapour phase. Someone examining the literature for calorific values might not always be informed expressly whether the value given is the HHV or the LLV. The calculation in the boxed area below addresses this point.

From [12], the hydrogen content of dry MSW from KL is 6.86%. The MSW is however burnt at a moisture content of 55%. One kilogram of the MSW as fired therefore contains:

$$(68.6 \times 0.45)\text{ g hydrogen} = 31\text{ g hydrogen or }15.5\text{ mol (expressed as }H_2)$$

$$\downarrow$$

15.5 mol of water on combustion

Using a value of 44 kJ mol^{-1} for the heat of vaporisation of water at 25°C, the heat released on the condensation of 15.5 mol of water at that temperature =

$$44 \times 10^{3} \times 15.5 \times 10^{-6}\text{ MJ} = 0.7\text{ MJ}$$

So for a calorific value in the range 10 to 15 MJ kg^{-1} the HHV and LHV differ by something like 5%

It is repeated that if the determination of the calorific value was in a bomb calorimeter it is CERTAIN that it corresponds to the HHV. If such information is not given an uncertainty of about 5% results. This is comparable to errors in the determination of the calorific value of MSW in a bomb calorimeter [10]. Errors would not be this large in the laboratory measurement of the HHV of a coal, where much more uniform samples for the calorimetric work can be obtained than can for MSW.

1.4 Constituents of MSW other than household waste

Local authorities will collect, in addition to waste from households, waste from some commercial premises. At present about 10% of the MSW generated in the UK is of trade rather than domestic origin [15]. Any waste incorporated into the MSW must be of comparable composition to household waste and must have no hazards additional to those of household waste. Obviously therefore, hospital waste would not be incorporated into MSW. It is reported in [15] that ‘commercial waste’ collected in London (UK) is as high as 64% in paper and cardboard and about 11% in plastics including plastic film used in wrapping. Litter from bins mounted in the street also finds its way into MSW, and debris from fast food outlets features strongly in this.

1.5 Carbon neutrality or otherwise of MSW as a fuel

Clearly some constituents of MSW are carbon-neutral and others are not. In the former category are paper and vegetable peel and in the latter are plastics. Commonly MSW is taken to be 50 to 70% carbon neutral. Because plastics have about twice the calorific value of cellulose their contribution to their heat release on combustion is disproportionate to their weight contents, a factor requiring thought when carbon dioxide emissions are being calculated.

1.6 Trade wastes

‘Waste from commercial premises’, discussed in the previous section, is distinct from ‘trade waste’. Trades and industries produce solid waste peculiar to their particular activities and processes. Such waste might, like MSW, be suitable for fuel use. Details of a few such wastes are given in the table below. Comments follow the table.

Trade or industry	Amounts of waste and calorific value
Furniture	1 million tonnes of lignocellulosic waste from furniture manufacture per year in the UK [16]. Calorific value ≈ 17 MJ kg^{-1}
Vehicle tyres	Tens of millions of tyres scrapped in the UK each year. Calorific value ≈ 30 MJ kg^{-1} [17]
Leather	20 million tonnes of leather waste per year in the UK Calorific value ≈ 20 MJ kg^{-1}
Citrus fruit products	5 million tonnes per year of orange peel produced in the US [18]. Calorific value ≈ 5 MJ kg^{-1}
Offices	80 million tonnes of waste paper per year in the UK [19].

Wood waste such as that described in row 1 is a good fuel, being of calorific value about 17 MJ kg^{-1} and, perhaps more importantly, of much more consistent composition than MSW and not as unappealing to work with. Combustion is not necessarily the destiny of such waste, however, as there are products obtainable from it including fibre board. Combustion of scrap tyres has proved difficult over the years, the reason being that the latex from which they are made releases copious amounts of volatiles on initial heating and this makes for a smoky burn. However, there is a revival of interest because of the carbon neutrality of latex, in particular of co-firing of shredded tyre waste with coal in power generation[2]. Citrus peel as a fuel has a strength and a weakness. The strength is that it is consistent in composition and in burning this makes for flame stability. The weakness is its low calorific value, due to the high moisture content. Sometimes a fuel is assessed on the number of times its own weight of saturated steam at one bar which it can raise, and one expects a value of not less than five for a coal obtained for steam raising. Citrus peel can only raise just over its own weight of saturated steam at one bar. A further disadvantage is that where there are large amounts of moisture in a fuel it is simply present before, during and after combustion. This means that large boiler furnace volumes are required to contain the vapour additional to the reactant and product gases.

Paper waste is ubiquitous and is of course a significant part both of MSW and of commercial waste. The figure in the fifth row of the table is for paper waste generated in offices. It provides a rationale for the rubric that sometimes accompanies an e-mail message that the contents should not be printed off unnecessarily.

1.7 Concluding remarks

The introductory chapter has given an account of the nature of MSW as a lead-in to subsequent chapters where burning, gasification and pyrolysis of MSW are described. The burning of MSW not merely to dispose of it but also to obtain some return on the heat is by no means new; the first such operation was at the NYC incinerator in the late nineteenth century. The scale of MSW production was pointed out, with emphasis, earlier in the chapter. Because of that and because MSW is partially carbon-neutral R&D into its fuel use is on-going.

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2. Municipal solid waste

Part II: Incineration

2.1 Introduction

We saw in the previous chapter that MSW tends to have a low natural bulk density, and to incinerate a consignment of MSW is to convert it to an ash having about a tenth of the volume. The ash is abundant and harsh, having a strong propensity to adhesion to plant surfaces which soon corrode as a result. The ash from MSW incineration contains metallic elements which might be recoverable. The most important function of incineration is of course destruction of micro-organisms. Obviously incineration of MSW results in carbon dioxide release, but there is a counter argument to this. Such wastes as paper and cardboard if taken to a landfill instead of being incinerated start to release methane by decomposition after time of the order of years, and it is well known that methane is a much more powerful greenhouse gas than carbon dioxide.

More often than not, incineration of MSW will be set up so that some of the heat is put to use, for example in hot water supply and district heating. The term Waste-to-Energy (WTE) then applies. It will be usual for heat from the incinerator to cross a boundary at a heat exchanger, in which case one fluid ‘belongs’ to the incinerator operator and the other ‘belongs’ to the purchaser of the heat. Nothing with mass changes hands, and energy has been sold simply and solely as such. At larger facilities (e.g., the Detroit incinerator – see next section) there will sometimes be steam turbines for generation of electricity which can be sold on. When MSW is processed to make a saleable fuel perhaps in pelletised form, that is refuse-derived fuel (RDF).

This chapter will be concerned with incineration and with extension to WTE. RDF will feature in the third of the group of chapters on MSW.

2.2 Examples incinerators and analysis of their operation

2.2.1 Preamble

Our purpose in this chapter will be best served by detailed examination of some major MSW incineration facilities and selections will be from different parts of the world. A waste incinerator has not fulfilled its entire role once it has destroyed the waste: the post-combustion gases have to treated before release into the atmosphere, and it is this aspect of waste incineration which most often attracts criticism and objection from environmental groups. Accordingly for each incinerator we review both combustion performance and pollutants in the combustion products will be considered.

2.2.2 The Detroit incinerator

What is believed to be the largest waste incinerator in the world is in Detroit[3]. It has been in service since 1989 [1]. It does not belong to the City, having been leased by it from a private owner throughout its existence, and the question of how much longer these arrangements will continue is currently the subject of debate and lobbying. Of Dutch design, the incinerator processes between 2200 and 3000 US tons of waste per day.

The Detroit incinerator was conceived during the presidency of Gerald Ford. His predecessor President Richard M. Nixon, during whose second term in office the 1973 oil embargo took place, had emphasised the potential of city waste as a fuel for electricity generation. The money to build the Detroit facility was raised in the 1980s [2,3], and by the time it came into service in 1989 the oil supply-and-demand situation was quite different from that in 1973. A view that the *raison d’etre* of the Detroit incinerator was expired by the time it opened for business therefore has at least limited validity.

The incinerator provides electricity for 30000 households in Detroit. It used to provide steam[4] for Detroit Thermal [4], suppliers of heat to about 100 buildings in Detroit’s central business district. Detroit Thermal now use natural gas instead to raise steam. A simple calculation apropos of these figures is in the boxed area below.

Taking the mid range of the daily amount of waste processed to be 2500 tonne and taking the calorific value to be 10 MJ kg^{-1}, the energy released in a day's incineration is:

$$2500 \times 10^3 \text{ kg} \times 10^7 \text{ J kg}^{-1} = 2.5 \times 10^{13} \text{ J}$$

If electricity generation is at 30% efficiency this becomes:

$$7.5 \times 10^{12} \text{ J}$$

Now the average domestic daily electricity consumption in the US [5] is approximately

$$30 \text{ kW hours} = 1 \times 10^8 \text{ J}$$

30000 homes will require:

$$10^8 \times 3 \times 10^4 \text{ J} = 3 \times 10^{12} \text{ J}$$

Order-of magnitude agreement is pleasingly evident in the calculation. The gap between the calculated figures presumably represents in part the steam that was formerly bought by Detroit Thermal and will now be on the market.

On the pollution control front, the incinerator facility experienced major difficulties only about a year after it came into operation [6] when on account of the amounts of mercury it was releasing into the atmosphere it was closed down by the authorities for a period of days. Permission to resume was dependent upon a commitment to install improved pollution control plant. The facility produces about 1000 tonne per day of ash. Difficulties with the ash from MSW combustion have already been described.

2.2.3 The Tuas South Incineration Plant (TSIP), Singapore

Tuas is an industrial zone in western Singapore. The waste incinerator plant there is the largest of four such plants in Singapore and receives household and industrial waste. Constructed by Mitsubishi and commissioned ten years ago, its nameplate capacity is 3000 tonnes per day. This puts it in the same 'league' as the Detroit incinerator considered in the previous section[5]. Electricity is generated [7] by means of a steam turbine using a Rankine cycle. This uses waste water from industrial processing, which is cleaned by membrane filtration before use. TSIP therefore does not draw on the potable water supply. The waste which the Tuas South facility receives is fairly low in calorific value, about 6 MJ kg^{-1} [8]. A reader will be aware from Chapter 1 that MSW can be twice this in calorific value. Calculations similar to those in the previous section reveal that 3000 tonnes per day of waste of calorific value 6 MJ kg^{-1} burnt to raise steam for entry to a Rankine cycle with 35% efficiency would generate electricity at approximately 75 MW. About a fifth of this is used at the facility and the remainder sold on. Electricity generation on a very much larger scale takes place at Tuas Power Station, a separate facility currently being expanded. This uses a variety of conventional fuels.

Two further points will be made in relation to TSIP. One is that corrosion in the boiler has at times been severe and this has been attributed [9] to hydrogen chloride arising from the burning of PVC in the fuel waste received. This of course is also a potential problem in relation to dioxins. The other point of interest is that, since metal components are not removed before admittance to the incinerator the solid residue contains both ash and 'slag', that is, metal possibly partly oxidised originating from the metal items such as cans in the waste. Iron in the slag is recovered with a magnet for recycling and the remainder disposed of with the ash. In the city state of Singapore space is at a premium, and the ash and slag from TSIP are in fact taken to an offshore landfill at Pulau Semakau. This also receives any MSW generated in Singapore not disposed of at one of the four incinerator plants.

2.2.4 The Gojogawa Incineration Plant, Nagoya Japan

A very detailed account of this plant is given in [10], and points can be gleaned which are of general interest. Japan relies almost entirely on imported fuel. She has no crude oil to speak of and although she has coal no longer mines it buying it instead from countries including Australia and Indonesia. One therefore expects that a waste incinerator which reliably produces electricity would be viable in Japan.

The Gojogawa plant, constructed over the period 1995 and 2004, is smaller than the incinerator plants discussed previously in this chapter. It receives 560 tonne per day of waste. Using the same figure for the calorific value of MSW which featured in the previous section it can be estimated that the plant will produce electricity at 12 kW. The actual value [10] is 14.5 MW.

Chemical analysis figures for the waste received at the facility under discussion are not available. However, dry MSW usually contains about 50% carbon and about 7% hydrogen. The calculation in the boxed area below develops this discussion.

560 tonne per day of waste as received equivalent to ≈ 400 tonne per day of dry waste
Supply per hour = 16.5 tonne of which:
8.25 tonne carbon
1.2 tonne hydrogen
moles carbon burnt per hour = $8.25 \times 10^3/0.012 = 6.9 \times 10^5$ requiring an equivalent number of moles of oxygen.
moles hydrogen (expressed as H_2) burnt per hour = $1.2 \times 10^3/0.002 = 6 \times 10^5$ requiring 3×10^5 moles of oxygen
Total oxygen requirement per hour = 10^6 mol
Total air requirement per hour = 4.76×10^6 mol
Volume at 1 bar 298 K = 120000 m^3
If say 25% excess air is used, volume of air per hour = 149000 m^3

Now we are told in [10] that there were three draft fans at the incinerator, and that their combined capacity is 188000 m^3(1 bar, 298K) per hour. The largest of the three provides for a variable delivery of air, the value having been incorporated into the combined figure being the maximum. It will therefore not be working at full capacity all the time, and there is likely to be a small degree of interdependence of the performance of the largest fan and those of the other two which are not themselves controllable. Having regard to such factors and also to approximations made in the composition of the waste, agreement to within about 20% of the specified and calculated air supply rates is a very good result.

Other features of interest at the Gojogawa incineration plant include removal of dioxins from the post-combustion gas by adsorption on to activated carbon. Sulphur dioxide, which of course forms an acidic solution with water, and hydrogen chloride are removed in the conventional way by neutralisation with lime.

2.2.5 Further examples

These are given in the table below. Comments follow the table.

Place	Details	Reference
Oahu, Hawaii.	≈1500 tonne per day of MSW processed, and 7% of the electricity for Oahu generated.	[11]
Nantes, France.	Up to 500 tonne per day. Electricity and heat sold on.	[12]
Port Talbot, Wales	30 tonne per day of MSW disposed of.	[13]
St Gallen Switzerland	≈ 125 tonne per day.	[14]
Stoke-on-Trent, England	≈ 500 tonne per day	[16]
Berlin, Germany	1400 tonne per day	[17]
Tokyo	The Shin Koto incineration plant, with a capacity of 1800 tonnes per day, is the largest in Tokyo	[18]

The facility at Oahu is believed to have a limited future. This is because landfill space for the ash is becoming used up. In France there are endeavours to dispel the idea that waste incineration is an unaesthetic or even sordid activity by introducing an artistic dimension. Part of the incinerator site at Nantes is given over to a display of modern sculpture. An incinerator close to Paris is illuminated after dark to give it visual impact, almost as if it were a cathedral! There have been difficulties with the Port Talbot incinerator (row 3 of the table), and the local authority which operates it has initiated legal proceedings against the firm which, under contract, built it. The figure for the St. Gallen facility represents only something like 2% of the MSW incinerated in Switzerland, where in 2000 its disposal at landfills ceased by law [15]. The Berlin facility is the primary MSW disposal route for that city, as in Germany since 2005 only incinerator residue can be land-filled, not untreated waste. The incinerator in Berlin predates by a few years perestroika and is in a state of obsolescence. Extensive upgrading and retrofitting are under way. The Shin Koto incineration plant (final row of the table) has recently been visited by officials from Hong Kong with a possible view to the building of one like it there.

2.3 Small-scale waste incinerators

Circumstances under which small-scale MSW incineration is required include remote communities and passenger shipping terminals. In the latter ‘household’ waste generated during a long voyage needs to be disposed of. As an example of the former, in Canada two separate settlements of indigenous people of the Cree race benefit from MSW incinerators built to meet their needs. These have capacities of respectively 3 and 8 tonne per day [19]. The same firm which supplied them has installed in the port of Belize an incinerator for waste from passenger ships. It can take a load of up to about 200 kg. Other situations where small incinerators for disposal of waste find application include military bases and mines.

2.4 Concluding remarks

In these days of concern on two fronts – depletion of conventional fuels and build-up of carbon dioxide in the atmosphere – incineration of MSW is at first consideration attractive. That it is ‘renewable’ nobody would deny and that it is largely carbon-neutral was shown in the previous chapter. In the 1880s, when oil and coal in the US were both very much growth industries, there was interest in ‘energy from waste’ and implementation of the idea in NYC as already noted. Yet at the present time whenever proposals to build an incinerator are made there is widespread opposition, as is the case in Leeds, England at the moment. One can be confident that in a country like the UK a newly commissioned incinerator facility will be state-of-the-art with all possible care and attention to emissions and to disposal of solid residue.

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3. Municipal Solid Waste

Part III: Pelletised forms

3.1 Introduction

Refuse-derived fuel (RDF) is as its name informs one waste substance destined for fuel use. Possible treatments of waste to make RDF are many and include Mechanical Biological Treatment which has brief coverage later in this chapter. This chapter is concerned with pelletising of MSW to make what approximates to a general-purpose solid fuel. Processes involved in the manufacture of such pellets include drying, shredding and 'densification'[6]. Over the decades there has been much endeavour in making RDF pellets but it has only ever been on a modest scale, RDF never having seriously challenged coal or wood. There is increased interest at the present time, partly because of the partial carbon neutrality of such fuels.

As we saw in an earlier chapter MSW has a very reasonable calorific value, more so if it is dried to make RDF. One difficulty with RDF is that heterogeneity of composition of MSW makes for variation of composition. Another is that RDF pellets tend not only to be high in ash but that such ash is often corrosive to combustion plant. Another is that the MSW as received for processing might well contain pathogenic bacteria: that was largely the motive for getting it out of households in the first place! These issues will be raised again when particular examples of RDF pellets are described.

3.2 Manufacture of RDF pellets

3.2.1 Principles

A good summary of what is involved in making pelletised RDF from MSW is given in [1]. The information relates to an RDF manufacturing plant designed and built by the Japanese concern Kawasaki. MSW as received is crushed and blast dried, that is, treated with air previously electrically heated. This also brings about deodorisation of the MSW. Metals, glass and any other non-combustibles are then removed and this is followed by shredding in readiness for pelletisation, a.k.a. the 'solidifying step'. This process is also referred to as 'densification' as noted in the previous section. In a suitable climate, the blast drying step can be replaced by solar drying.

Presses for making RDF pellets 'evolved' from those designed for making animal feed in the form of pellets [2]. It is described in [3] how in the production of RDF pellets of cylindrical shape and of 15 mm diameter a force of 50 kN was applied axially. It is easily shown that the pressure experienced by the pellets during processing would have been:

$$50 \times 10^{3}\ \mathrm{N}/[\ \pi(7.5 \times 10^{-3})^{2}]\ \mathrm{m}^{2} = 280\ \mathrm{MPa}$$

which is about half the design stress of a typical stainless steel [4]. RDF pellets will usually require a binder. In contrast to coal briquetting technologies which use an organic substance – either petroleum residue or a starch – as a binder, RDF pellet manufacture often uses an inorganic binder. Calcium hydroxide is a common choice. Where the waste from which the RDF was made contained large amounts of PVC a further inorganic additive might be used to fix the chlorine as a metal chloride in the ash on combustion, preventing its release as hydrogen chloride into the atmosphere. Magnesium hydroxide can be used as such an additive.

RDF is expected to have a calorific value of the order of 12 to 15 MJ kg^{-1}. It is sometimes possible to raise the calorific value of RDF pellets by blending, prior to application of pressure, with a suitable trade waste such as carpet waste. Peanut shells and rice husk have also found such application. The term c-RDF, where ‘c’ stands for composite, is used to describe such fuels. Approximately synonymous is REF, ‘in-origin recycled fuel’.

RDF pellets might be used as the sole fuel for a particular plant or, increasingly frequently, co-fired with a conventional fuel. Details of combustion of RDF, with examples, will be discussed starting with the table below.

3.2.2 Selected scenes of RDF manufacture

Location	Details	Ref.
Andhra Pradesh, India	RDF pellets as fuel for electricity generation. Calorific value 12 to 13 MJ kg^{-1} Ash content 20%	[5]
Herhof plant, Dresden, Germany	Pre-treatment by 'aerobic digestion' before pelletisation (see below). Pellets of calorific value 15 to 18 MJ kg^{-1}.	[7]
Kahada-Okuise RDF plant, Japan.	Calcium hydroxide binder used. Pellets of calorific value 18 to 20 MJ kg^{-1}	[7]
Istanbul, Turkey	Pilot study into pelletised RDF production.	[8]
Greve in Chianti, Italy	RDF pellets of calorific value 17 MJ kg^{-1}.	[9]
Stockholm, Sweden	CHP from fuels including REF pellets.	[10]

Very interestingly, reference [5] gives a value for the energy-return on energy invested (EROEI) for the RDF of 10 to 15. According to recent thermodynamic theories of energy-return-on-energy-invested for conventional fuels [6], this EROEI would apply to crude oil obtained from a well having a depth of about 2000 m. The fact that RDF is made from MSW which has to be disposed of would have the effect of raising the EROEI. This is because whatever energy would have been involved in taking the waste to a landfill instead of processing it to RDF can be subtracted from the 'energy invested'.

At the Herhof plant described in row two of the table, following removal of non-combustibles there is treatment in air at 60°C for a week in a process called aerobic digestion. This is in effect natural composting accelerated by temperature. At the Herhof plant the material after aerobic digestion has a fluffy nature and it is this which is pelletised. In some applications the fluff is used as a fuel as obtained without pelletising. Comparing the calorific values of the pellets in rows two and three of the table, the indication is that the aerobic digestion at the Herhof plant has had a marginally unfavourable effect on the calorific value. If this is so (and much more evidence would be needed for the 'indication' to become even a tentative 'conclusion') it is not difficult to explain. The prolonged treatment at 60°C would have involved loss of low-temperature volatiles such as methanol and formaldehyde which, had they been devolatilised in burning instead of in pre-treatment, would have enhanced the calorific value.

In the pilot study in Turkey described in the next row, the moisture content of the pellets was 25%, not unusually high for such a fuel but too high for the intended use of the pellets. The difficulty with high moisture is not its effect on the flame temperature (although there certainly is such an effect) but the fact that evaporated water adds to the space required in a furnace (as noted in a previous chapter) and in flue gas removal. This makes for difficulties if, as is likely to be the case, the RDF pellets are to be used in plant previously taking a conventional fuel. It was mentioned in Chapter 1 that MSW, in raw or in pelletised form, is not necessarily destined for burning but can be gasified, to make a fuel gas which is itself burnt. Again a 'sneak preview' of a later section of the book is necessary as the gasification of waste is a wide topic requiring in a text such as this major treatment. That being said we note two points at this stage. First, a significant proportion of the RDF pellets at Greve in Chianti (row five of the table) are gasified to make a fuel gas. Secondly, whatever the effects on the EROEI of the conversion to gas such a gas has many advantages over RDF pellets including the obvious one of its giving a cleaner burn. The point about the excessive gas volume caused by water inherent in the fuel is noted in [10], which is concerned with a CHP plant in Sweden which draws on a miscellany of fuels according to price and availability. These include wood waste from demolition.

3.2.3 Carbon neutrality issues

Although pelletisation of MSW to make pelletised RDF is not new, much research activity into it in the last few years has found its way into peer-reviewed journals. The motivation for the work has been the stretching of conventional fuels, and two factors have necessitated this. One is that many countries have either reduced their coal production (e.g., the UK) or ceased coal production altogether (e.g. Japan). As already noted Japan relies on imports from countries including Australia and Indonesia and the UK produces of the order of 20 million tonnes per annum for the domestic market. A century ago she was producing about five times this. A renaissance of coal production and utilisation is by no means off the agenda, but if it occurs it will not be a simple 'return to the past'. Disused mines cannot be brought back into production at a moment's notice, and increased stringency of safety standards since coal production ceased in the UK will make for expensive infrastructure if mines are reopened. Also, the future for coal is not its burning as such but its gasification in what is sometimes called 'BTU conversion'. The second factor having stimulated recent research into RDF combustion has been touched on already in this book: its partial carbon neutrality. Another point mentioned earlier is that RDF-coal co-firing is expanding and enabling such organisations as electricity producers to meet renewables obligations.

It is necessary to expand upon the matter of the carbon neutrality if we are knowledgeably to examine recent work on coal-RDF coal firing. What is required to meet carbon dioxide reduction requirements is not necessarily a reduction in total carbon dioxide release but a reduction in fossil fuel derived carbon dioxide release. Carbon dioxide released on the burning of a carbon-neutral substance was in the fairly recent past carbon dioxide in the atmosphere, so to burn a carbon-neutral fuel is to put carbon dioxide back where it came from. Having regard to the uptake of carbon dioxide by vegetation, return to the atmosphere of carbon dioxide from carbon-neutral fuels causes no net increase in the CO_2 level. By contrast, carbon in coal was not on any time scale of interest carbon dioxide in the atmosphere, so to burn coal adds to the CO_2 level of the atmosphere. The present author has published elsewhere (e.g. [11], [12]) calculations which show that when in a combustion process a carbon-neutral fuel such as wood waste is fully or partially substituted for a bituminous coal the result, other things being equal, will be an increase in the total carbon dioxide release. The important difference is that carbon dioxide resulting from the carbon-neutral fuel, unlike that resulting from coal, makes no net contribution to the CO_2 level of the atmosphere as explained above.

3.3 Performance issues

3.3.1 Preamble

This section will take analysis and other data for representative RDF pellets and use them in calculations relevant to performance. The example of pelletised RDF used is taken from reference [13]. It originates in Nagoya, Japan, and information on it taken directly from [13] is given in the table below. It is clear that this RDF is one of fairly low moisture and correspondingly good calorific value and is a most suitable choice to represent RDF pellets generically in the calculations which follow.

Property	**Value**
Calorific value/MJ kg^{-1}	18
Moisture content %	11.1
Carbon content % d.b.*	46.9
Hydrogen content % d.b.	6.75
Oxygen content % d.b.	40.8
Nitrogen content % d.b.	0.84
Sulphur content % d.b.	0.19

3.3.2 Air requirement on burning

This is calculated in the shaded are below.

Per kg of fuel burnt:

469 g of C = 39 mol C → 39 mol CO_2 on burning requiring 39 mol of O_2

67.5 g of H = 33.75 mol if expressed as H_2 → 33.75 mol H_2O requiring 17 mol of O_2

Total moles of O_2 in the above equations = 56

The fuel's own oxygen content per kg expressed as moles O_2 = 12.8

Oxygen requirement = (56 – 12.8) mol = 43 to the nearest whole number

Accompanying nitrogen = 43 × 3.76 mol = 162 mol

Total air required to burn 1 kg of the RDF pellets = 205 mol or 5.9 kg

If say 30% excess air were used total requirement = 7.7 kg

The above follows the procedure for fairly routine 'combustion calculations' for coal and oil, extending the ideas to RDF pellets. A reader should note the following.

i. The factor of 3.76 by which the molar oxygen requirement is multiplied is the quotient 79/21, in which the numerator and denominator are the percentages molar basis respectively of nitrogen and oxygen in air.
ii. Oxygen in the fuel before burning signifies fuel already oxidised, so it has to be subtracted from the oxygen requirement.
iii. The sulphur in the RDF will go quantitatively to sulphur dioxide, a point to which we shall return when discussing emissions. The oxygen requirement for this is however so low that it can be neglected in the above calculations.
iv. Excess air to a degree of about 30% would be common in such an application.

The conclusion then is that a kilogram of the RDF pellets would require six kilograms of air for combustion. In addition to having calculated this result we can claim to have done at least a partial mass balance on the process. This we continue in the calculation of the composition of the flue gas.

3.3.3 Composition of the flue gas

Calculation of flue gas composition is in the shaded area below and begins with information from the previous calculation.

Gas resulting per kg pellets burnt:

CO_2 39 mol

Product H_2O vapour 34 mol

H_2O vapour from the fuel's own moisture content 6 mol

N_2 211 mol

O_2 12.9 mol

Total 303 mol of gas per kg of the pellets burnt. Re-expressing as percentages:

CO_2 13%

H_2O 13%

N_2 70%

O_2 4%

Once the gas had cooled say to 25°C the water would cease to be in the vapour phase and the total number of moles would be 263 per kg of the RDF pellets burnt[7]. Now at 25°C and 1 bar pressure:

$$1\ \mathrm{m}^3 \text{ of any gas or gas mixture contains approximately 40 mol}$$

therefore the volume of gas produced in the burning of 1 kg of the pellets is:

$$263/40 = 6.6\ \mathrm{m}^3$$

It is hoped that a reader might use these figures in order to enlarge upon those given for particular RDF facilities in the table previously presented. The calculations are extended below to the adiabatic flame temperature.

3.3.4 Adiabatic flame temperatures

The adiabatic flame temperature is the temperature attained when all of the heat released is retained as enthalpy (sensible heat) in the reaction products. It is an upper bound on actual realisable flame temperatures. The adiabatic flame temperature for the RDF pellets under consideration is calculated in the shaded area below. It first has to be pointed out that the adiabatic flame temperature is usually calculated for stoichiometric conditions, that is no excess air. The calculation below is for such conditions.

The post-combustion gas for stoichiometric conditions has the following composition:

CO_2 39 mol H_2O 40 mol N_2 162 mol O_2 zero

Total 240 mol

On a fractional basis this is:

CO_2 16% H_2O 17% N_2 68%

The heat capacity of the gas is then:

$0.16C(CO_2) + 0.17C(H_2O) + 0.68C(N_2)$

where C denotes the heat capacity (J $K^{-1}mol^{-1}$) of the respective constituent gases. We use the following values.

CO_2 60 J $K^{-1}mol^{-1}$

H_2O 50 J $K^{-1}mol^{-1}$

N_2 36 J $K^{-1}mol^{-1}$

The gas resulting from burning of 1 kg of the RDF pellets therefore has heat capacity:

$$[(0.16 \times 60) + (0.17 \times 50) + (0.68 \times 36)] \times 240 \text{ J K}^{-1}$$

$$= 10220 \text{ J K}^{-1}$$

In the table in section 3.3.1 we are told that 1 kg of the RDF pellets release on burning is, to the nearest whole number, 18 MJ. The adiabatic temperature rise is then:

$$(18 \times 10^6/10220 \text{ K} = 1760 \text{ K}$$

This is the temperature rise in K or equivalently in ^oC. Starting with fuel and air at 300K the actual flame temperature would therefore be 2060 K.

The heat capacities in the calculation are for a single temperature. A more rigorous treatment would incorporate the heat capacities as a function of temperature. That is probably the principal source of error in the above calculation which nevertheless has given about the value expected. We note [14] that the adiabatic flame temperature of methane in air under stoichiometric conditions is 2222^{o}C (2495K). Very close comparison would not be helpful since the calculation herein for RDF is an approximate one. There is also a source of error in the use of a single value for the calorific value from [13] when this in fact will have a significant plus-or-minus on it. Even so the following conclusion can be drawn: in terms of combustion temperatures reached RDF pellets can hold their own against conventional hydrocarbon fuels.

3.3.5 Emissions

Many recent research papers on RDF pellets are concerned with emissions during combustion. Most of them are concerned with RDF-coal co-firing which as stated previously is becoming more prevalent and which will be discussed in the next section of this chapter. In considering RDF alone from the emissions angle we return to the information in [13] which was used in the previous section and note that the sulphur content of the pellets in [13] was 0.19%. Now we showed in the previous calculations that 6.6m^3 of post-combustion gas, measured at 298K and 1 bar, resulted from the burning of 1 kg of the fuel under conditions such that there was total condensation of product water.

1 kg of waste burnt contains 1.9 g S

$\downarrow$

3.8 g SO_2 or 0.06 mol

Number of moles in 6.6 m^3 = 260 approx.

p.p.m. $SO_2 = (0.06/260) \times 10^6 = 230$

We first note that it is in general correct to equate the moles of elemental sulphur in the fuel to the moles of sulphur dioxide produced. In any fuel there is a stoichiometric conversion to sulphur to sulphur dioxide on burning even if conditions are fuel-rich. The one exception which is often cited is that in certain coals sulphur dioxide once formed can be further oxidised and become sulphates in the ash by combination with calcium or sodium. Having regard to the fact that the RDF in [13] does contain calcium amongst its 'inorganics' such behaviour is possible here. It would be straightforward to calculate how much sulphur at most could be fixed in this way from the calcium content, the rest becoming sulphur dioxide.

The sulphur dioxide concentration of 230 p.p.m. would need to be reduced, by scrubbing of the flue gas or by use of lime, by the factor estimated below.

230 p.p.m. becomes ≈ 0.2 p.p.m. on dispersion. For emission standards and ambient standards to be about the same, a drop to not more than 1 p.p.h.m is required[8].

Comparing the two values:

1 p.p.h.m./20 p.p.h.m. = 0.05

meaning that 95% of the sulphur dioxide will need to be removed.

The above result does not make for difficulties in operation. Plenty of coals are as high in sulphur as the RDF pellets in [13] as are some heavy fuel oils.

Whereas sulphur is quantitatively converted to sulphur dioxide on combustion, fuel nitrogen is converted quantitatively to nitrogen gas N_2. A very small proportion which might hardly reveal itself in a routine mass balance calculation will go to NO and NO_2, jointly referred to as NO_x. This is called fuel NO_x and contrasts with thermal NO_x which is due to reaction of nitrogen and oxygen in the air. Thermal NO_x occurs only at combustion temperatures of about 1300°C or higher. The role of NO_x in atmospheric pollution has been described by the author elsewhere [15]. NO_x release into the atmosphere has to be controlled and regulated, and this applies to RDF and 'conventional' fuels alike.

Where RDF contains major amounts of chlorine, as it will if the MSW from which it is made contains PVC, calcium can be incorporated to trap it as calcium chloride preventing its release as HCl. An example of this is discussed in section 3.4.

3.4 Coal RDF co-firing

The table below summarises three recent activities in RDF pellet-coal co-firing, both investigative studies and plant which is 'up and running'. Comments follow the table.

Reference	Details
[16]	RDF pellets of calorific value 24 MJ kg^{-1} made from paper and plastic waste co-fired in a fluidised bed with a bituminous coal of calorific value 21 MJ kg^{-1}, also paper sludge and tyre-derived fuel[9]. Five large-scale tests performed each of one week's duration.
[17]	Slough, England. Coal and pelletised waste co-fired in a fluidised bed for electricity generation. Heat contribution 40% from the waste 60% from the coal.
[18]	RDF pellets and coal co-fired in a fluidised bed reactor. Inclusion of $CaCO_3$ to trap chlorine.

In interpreting the results in reference [16] we first note that a 'cocktail' of three waste-derived fuels and one conventional one was used. The very high calorific value of the RDF pellets is due to their high plastics content and their low moisture content. On burning of this sulphur dioxide levels of about 200 p.p.m. in the flue gases were observed. The bed operated at about 900°C, too low for there to be thermal NO_x. Measured NO_x levels of up to 80 p.p.m. in the flue gas were therefore fuel NO_x entirely.

At the plant at Slough which features in the second row of the table, some of the waste fuel is RDF pellets and some consists of small cubes – typically 3 cm side – of compressed cellulosic waste. The advantage of cellulosic waste is that it is entirely carbon-neutral whereas RDF from MSW is only partially so. Accordingly electricity from the plant is sold to electricity producers to enable them to meet their non-fossil fuels obligations. Sulphur dioxide produced at the Slough facility is removed by inclusion of limestone in the fluidised bed. The bed temperature is too low for thermal NO_x to be formed.

When calcium carbonate is being use to trap chlorine as in the study described in the third row of the table, the efficacy of the trapping can be assessed in the following way. The amount of chlorine in the waste-derived fuel is measured and, in experimental trials, amounts of calcium (as carbonate as noted) in various multiples in molar terms of the chlorine are injected into the combustion system. The ash can be analysed for chlorine, and that expressed as a function of the molar ratio of calcium to chlorine (Ca:Cl). The higher the chlorine level in the ash the more effective the calcium has been in removing it from the gas phase. In [18], the chlorine content of the ash was 0.1% when there was no calcium carbonate injection at all, rising to ≈ 0.14% for Ca:Cl = 5, to ≈ 0.2 for Ca:Cl = 10 and to ≈ 0.25 for Ca:Cl = 15. A large excess of the calcium carbonate is therefore needed for a good result.

We observe from several of the examples of waste-derived fuels examined so far in this book that fluidised beds are often preferred over, for example, grate combustion in the burning of wastes. Fluidised beds are often used for poorer fuels. The value of the fluidised bed has been explained to countless students at Aberdeen by the following analogy. If an electric iron is set at too high a temperature for the fabric to which it is to be applied it will create a hole in it. However, if air at the same temperature as the iron is directed at the fabric it is much less likely that damage will result. With the hot iron heat transfer is by conduction: with the hot air it is by convection. In the latter case the fabric will never get to the air temperature because of heat transfer from itself to the surroundings leading to an equilibrium temperature well below that of the air. In a fluidised bed heat to the fuel particles is received by conduction from the fluidised material which will consist of inert particles, often sand. This makes for a rapid heating rate of the fuel particles to the acceleration of combustion.

3.5 Concluding remarks

It has never happened on a wide scale that RDF pellets have become a general-purpose solid fuel for distribution as, for example, coal briquettes have. Where we are seeing major activity into RDF pellets is in electricity generation where three factors are in their favour: their low cost in comparison with oil and coal, their partial carbon neutrality and the advantages of RDF production over landfill disposal of MSW. So will producers of RDF pellets ever be, on a large scale, stockpiling before transportation of the pellets by road and rail to users? The need for safe storage practices with large volumes has been recognised in a program of research in Japan into self-heating in stockpiles [19]. Additional to self-heating is the possibility of hydrogen production from RDF by micro-organisms.

The idea that RDF pellets might be exported from one country to another cannot be dismissed, as raw MSW not even destined for fuel use is sometimes transferred between countries. A good deal of the waste which goes to landfills in the US state of Michigan is imported there from the Canadian Province of Ontario. Payment for that is from Canada to the US so it can be described as a ‘negative export’ from Canada. That RDF pellets should ever become a major ‘positive export’ is at first consideration unlikely in that no country is short of the raw MSW from which they are made. This will not however necessarily preclude international trade in RDF pellets, as RDF pellets manufactured with close attention to quality are far superior to raw MSW in fuel applications. That a country should purchase high-quality RDF pellets whilst disposing of its own MSW by simple incineration or landfill is no more anomalous than transport of raw waste between Canada and the US for landfill disposal which, as we have already noted, is currently taking place.

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4. Miscellaneous Waste-Derived Solid Fuels

4.1 Introduction

‘Waste-derived solid fuels’ are legion and a revival of interest in them is expected as greenhouse gas emissions and depletion of conventional fuels continue to loom so large in world affairs. Some of the most important ones will be discussed in turn in this chapter, starting with tyre waste.

4.2 Scrap tyres

4.2.1 Preamble

The US produces hundreds of millions of scrap tyres in a single year and the UK tens of millions. Both the natural latex and any incorporated polymer are combustible and calorific values are high, sometimes in the neighbourhood of 40 MJ kg^{-1}. It is widely known that when tyres are burnt, either simply to destroy them by incineration with no return on the heat or in fuel applications, the high volatiles content of the constituent materials makes for smoky burning as noted in an earlier chapter. There is therefore a need for excess air and close attention to particulate release. Even so tyre-derived fuel (TDF) usage is major in many countries. Also, there is co-firing of tyre waste with conventional fuel as there is of RDF with conventional fuel. Waste tyres, like RDF derived from MSW, are partially carbon-neutral. The latex part is carbon-neutral but not of course any polymer within a tyre manufactured from petrochemicals.

4.2.2 Selected examples of TDF usage

By TDF usage in this section we mean TDF alone: co-firing will be discussed subsequently. The information is in tabular form below and is followed by comments.

Reference	**Details**
[1]	About 45 Portland cement production facilities in the US using TDF fuel at the present time.
[2]	Electricity generation in Sterling CT at 31 MW level with TDF. Electricity sold for general distribution.
[3]	Electricity generation in the English midlands at 25 MW level with TDF as sole fuel.
[4]	26 million scrap tyres used as fuel each year in the US pulp and paper industry. Shredding of the tyres necessary.
[5]	> 10 million tyres used as fuel for industrial water heating annually in the US.

The manufacture of Portland cement requires kiln temperatures as high as 1400°C and that TDF should have found application is not surprising. There is the bonus that some of the steel belting in the tyres contributes to the iron content of the product. It is recorded in [1] that Japan uses about 20 million tonnes of TDF in cement kilns annually. Many other countries including Germany, the Netherlands and Australia use TDF in cement kilns. The electricity utility at Sterling CT uses either whole or shredded tyres and is a 'dedicated TDF-to-energy' facility. The only other such facility in the US at the present time is the Modesto plant in Westley CA, which produces at 14MW.

In the pulp and paper industry (row four) shredding is required before tyres can be used as waste because the steel content of the tyres would otherwise cause slag formation in an unacceptably high degree.

4.2.3 Other factors in the use of TDF

The topic of TDF-coal co-firing was anticipated in the previous chapter; reference [16] therein, contents of which were summarised in one of the tables, was concerned with firing of waste-derived fuels including RDF with bituminous coal. As we have seen previously TDF has a calorific value if anything a little higher than that of a typical bituminous coal (although it would of course be possible to select a particular TDF and a particular coal such that the reverse was true). Hence where RDF is substituted for a bituminous coal it is on approximately a one-to-one weight basis. Reference [6] provides calorific values for fourteen examples of TDF, and they range from 29.2 to 37.9 MJ kg^{-1}. The mean of those is 33.6 MJ kg^{-1}. By way of a single illustrative example, this is about 10% higher than the value for a typical Pittsburgh coal. In countries including Turkey where there is much lignite – low rank coal having a calorific value as fired of 15 to 20 MJ kg^{-1} – there is some interest in TDF-lignite co-firing in which case the TDF will be by far the superior fuel in terms of calorific value.

Much of the research activity into coal-RDF co-firing is into emissions; when it is proposed to introduce co-firing limits in SO_2 and NO_x releases, set by regulatory bodies, have to be complied with. Reference [6] also gives sulphur contents for each of the TDF fuels and these range from 1.19 to 1.85%. This sulphur content in a <u>coal</u> would attract a penalty in pricing, and a disadvantage of TDF is its inevitably high sulphur content. It arises of course from vulcanisation in the manufacture.

4.3 Wood waste

4.3.1 Preamble

Wood is an important fuel in these times, as indeed it was over 100 years ago. It was surprisingly late – circa 1890 – that wood fuel usage in the US was exceeded by coal usage. A distinction has to be made between wood grown as fuel and wood waste diverted to fuel use. There has been an increase in the former by way of the ‘short rotation coppice’ and the like over the last few years. This book is however concerned only with the latter, wood waste put to use in combustion plant. The basis of the carbon neutrality of wood and the results of coal-wood co-firing were explained in a previous chapter. There are many forms of wood waste. Obvious ones are sawdust and shavings. Long before the current trend towards use of wood fuels there was use of wood as a supplementary fuel in power generation in those parts of the US with a major furniture industry. Teak products are a manufactured on a large scale in Thailand and many a tourist to that country has departed with a souvenir made of teak. Again, before wood fuels became prevalent teak waste found fuel application in Thailand. Increasingly important at the present time is the use of forest thinnings as a fuel. Woody debris from the forest floor is sometimes removed as a forest fire control measure, and if such debris can be put to fuel use in steam raising or whatever so much the better. It is of course carbon neutral, and in those terms there is a further benefit from fuel use. If wood waste of any sort is taken to a landfill it will, after time of the order of a few years, start to release methane as a decomposition product[10]. Methane is of course a much more powerful greenhouse gas than carbon dioxide.

Seasoned wood has a calorific value of about 17 MJ kg^{-1}. One performance criterion for a fuel is how many times its own weight of saturated steam at 1 bar it can raise. The comment was made in an earlier chapter that citrus peel can only raise just over its own weight of steam in that condition. This point is examined for wood waste in the boxed area below.

From [7] or equivalent:
specific enthalpy of liquid water at 25°C = 104.8 kJ kg^{-1}
specific enthalpy of water vapour at 100°C = 2675.8 kJ kg^{-1}
heat required to convert 1 kg of liquid water at 25°C steam at 100°C =
$(2675.8 – 104.8) \times 10^{-3}$ MJ = 2.6 MJ
weight of steam in this condition which could be raised by 1 kg of wood =
(17/2.6) kg = 6.5 kg.

4.3.2 Electricity generation from wood waste fuel

We focus on the US for facts and figures on this. The 2005 figure for electricity production in the USA from biomass waste is 54160 GWh [8] , which converts to a generation rate of ≈ 6000 MW. The consumption of electricity in the US in 2005 was 3816000 GWh, so the percentage provided by biomass waste is:

$$(54160/3816000) \times 100 = 1.4\%$$

Note that targets in the US for electricity from renewable sources is 12%. Even if the calculated above figure for 2005 has doubled by the time this is being written it will fall well short of 12%. If energy crops, distinguished from wood waste by the fact that they are grown expressly for burning, are factored in the gap will close to some extent. Even then isothermal methods of making electricity, including wind farms, will have a major role to play.

4.4 Selected cellulosic wastes other than wood and paper

Wood waste has been considered in this chapter and waste paper received significant attention in Chapter 1. There are many other cellulosic waste materials, and what distinguishes these from wood is the absence of lignin, hence the perhaps preferable term 'lignocellulosic' for wood. Some other cellulosic wastes which have found fuel use will be discussed in this section.

4.4.1 Bagasse

Bagasse is sugar cane residue, consequently occurring in such places as Fiji and northern New South Wales. It is used on site as a fuel for the sugar mills and has a significant propensity to self-heating which has been the subject of investigations by the present author [9] amongst others. Bagasse does however sometimes find fuel use external to the scene of its production. It is a fibrous material, of suitable consistency for fuel use. It is better than raw MSW for fuel use, being of more uniform composition and much lower in ash. It is composed of cellulose and hemi-cellulose and its calorific value is around 15 MJ kg^{-1}.

In Brazil there are proposals for electricity generation from bagasse [10]. This will ease the present heavy dependence of Brazil on hydroelectric power. A case for using bagasse as fuel for thermal generation of electricity will presumably have to be made on the basis of its carbon neutrality, as Brazil is a major oil producer[11] with extensive refining capacity so heavy residual fuel oil will be the obvious choice for electricity production.

Bagasse can be made into briquettes or into pellets for combustion use; there is significant interest in the former in Kenya [11]. When pellets made from bagasse originating in Brazil and in Cuba were studied on a comparative basis [12] the most obvious difference was ash content: 1.5% for the Cuban and 5.5% for the Brazilian.

4.4.2 Rice husks (a.k.a. rice hulls)

The table below gives details of some combustion applications of rice husks.

Reference	**Details**
[13]	Proposals for expansion of rice husks as fuel in Peru.
[14]	Proposals for electricity generation in Vietnam with rice husks as fuel.
[17]	Significant use of rice husks as a boiler fuel throughout India.
[18]	Feasibility study into power generation at up to 6 MW in Bangladesh with rice husks as fuel.
[19]	About 3 million tonnes per year of rice husks produced in the Philippines.

Peru (first row of the table) produces rice husks in annual quantities of the order of megatonnes. Traditionally some has been burnt directly in the brick industry and the remainder disposed of in ways which would not be acceptable in some countries, for example simply by burning out of doors or by dumping in a river. Consequently there have been endeavours to introduce fuel use of rice husks in Peru. The need for responsible disposal of rice husks makes them a fuel of negative financial value, a term commonly encountered in discussion of waste materials as fuels. This simply means that their disposal incurs a cost. However, the negative financial value can sometimes be offset by carbon credits generated if a fuel such as rice husks, which is carbon-neutral, is substituted for a fossil fuel.

It might at first consideration be surprising that in Vietnam (row two) rice husks would be pressed into service as a fuel as the country has large amounts of oil. What it does not have is an adequate refining and distribution infra-structure. The first refinery in Vietnam began operations as recently as 2009 [15] and its capacity – about 150000 barrels per day – therefore represents the entire refining capability of Vietnam at the present time. There are similar proposals for Thailand [16], with Japanese input. In spite of the instability of its regime, Thailand does attract Japanese investors at present. That there is rice husk usage in the Indian subcontinent is not surprising: rows three and four of the table give examples. Some of the rice husks produced in the Philippines become fuel and there are measures in place to increase fuel usage to the elimination of existing highly crude methods of disposal. The cellulosic fuel for which the Philippines is particularly noted is however coconut waste. A World Bank study has indicated that 20 MW of power could be generated in the Philippines from coconut waste fuel [19]. Reference [20] gives the 2005 electricity consumption of the Philippines as 53.67 billion kW hours. Converting to a rate of generation:

$$[53.67 \times 10^{12}\ \text{W hour}/(365 \times 24)\ \text{hour}] \times 10^{-6} = 6000\ \text{MW}^{12}$$

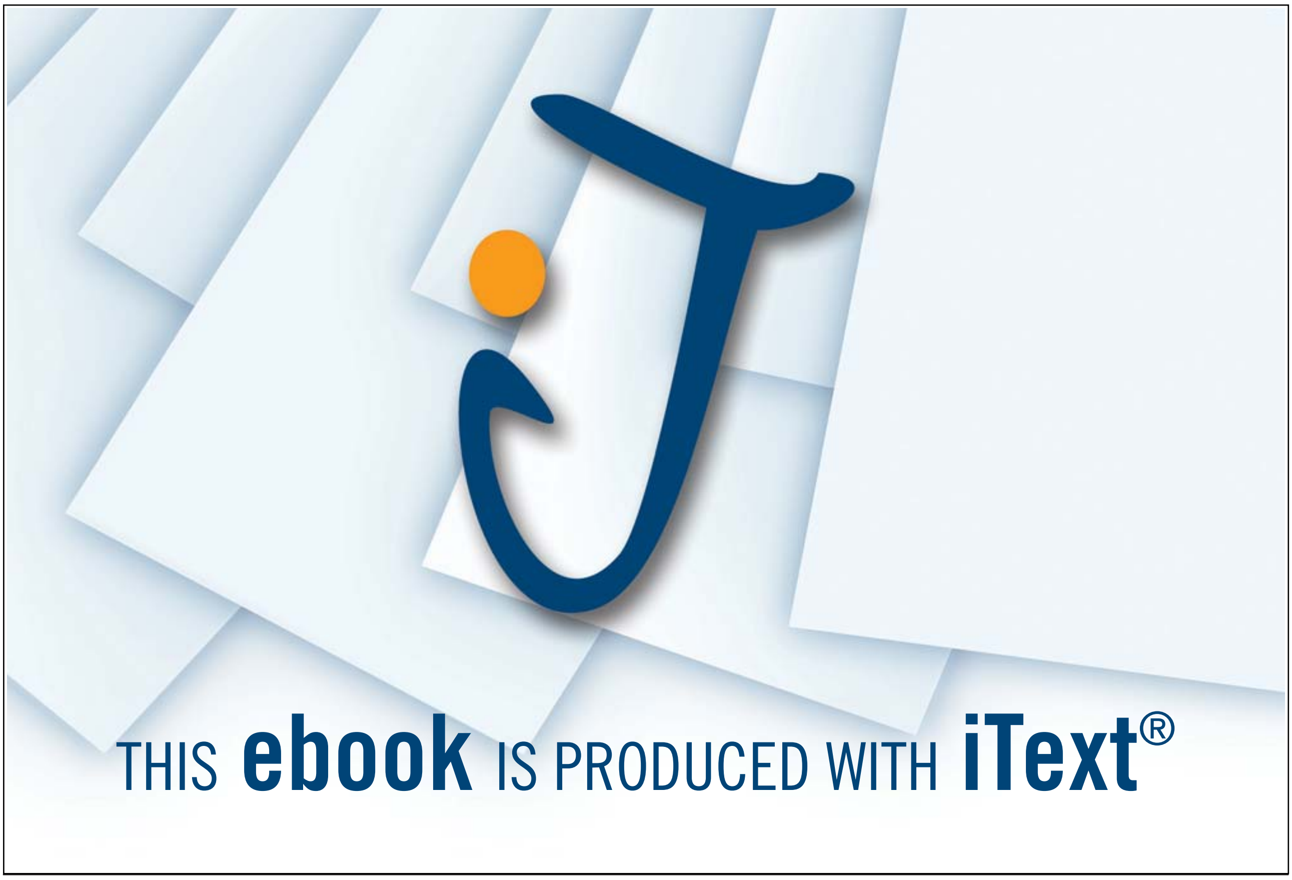
which is well above what, according to the World Bank study referred to, could be produced from coconut waste.

4.4.3 Cotton waste

There has for a long time been interest in cotton waste as a fuel in countries including Paraguay. There is current interest in the US of cotton waste fuels originating in states including LA, NC and AZ. It is reported in [22] that technologies for pelletising cotton waste are advancing. Blending of the cotton waste with a small proportion of cottonseed oil raises the calorific value of the pellets to 21 MJ kg^{-1}, higher than that of wood (except for a few woods exceptionally high in resin) with the bonus that the oil acts as a binder.

The matter of the EROEI of fuels has previously been raised in this book, and information relevant to that for a particular cotton waste fuel originating in Arizona is given in [23]. The following is taken from [23]:

> *Energy required to harvest the stalks averaged 9.2 kWh/t (12.1 hp-hr/ton) for the baling system, and 8.6 kWh/t (11.4 hp-hr/ton) for chopping and moulding. Specific energy*[13] *of the harvested stalks averaged 18.6 MJ/kg (7983 btu/lb)*



and these data are examined in the shaded area below.

Energy required to produce a tonne of the waste fuel =
(9.2 + 8.6) kWh = 17.8 kWh = 64 MJ
Heat released on burning a tonne = 18.6×10^3 MJ
EROEI = 290

This is a remarkably high EROEI: it is highly unlikely that it is matched by any crude oil produced in the early 21st Century (although values higher than that were possible for crude oil in the 1950s and further back). It is of course based only on one set of data[14] nor does the author wish to argue from the particular to the general. Even so the conclusion that a high EROEI can be expected from well managed production of cotton waste fuels is reasonable. EROEI is an energy quotient and attempts to express it in a financial paradigm are unsound. That being understood, the financial basis of cotton waste fuel usage is strengthened by the fact that carbon credits are generated and this is relevant to the overall viability.

We conclude this discussion of cotton waste with a reference [24] to a very recent study of cotton stalk combustion in a fluidised bed. Cotton stalk fuel was admitted at 35 kg hour^{-1} to the bed, which produced 0.2 MW of heat. In the limit of adiabatic conditions the calorific value of the fuel can be calculated as:

$$0.2 \times 10^6 \text{ J s}^{-1}/(35/3600) \text{ kg s}^{-1} = 20.6 \text{ MJ kg}^{-1}$$

which since some heat losses must in fact have occurred is an underestimate of the calorific value.

4.4.4 Further examples

The cellulosic fuels selected for discussion in this text have been wood, bagasse, rice husks and cotton wastes. There are of course very many other examples : amongst the better known are straw, peanut shells and coconut waste. Reference [25] gives a value of about 300000 for the total known number of plant species, and according to another source [26] cellulose is the most abundant organic substance on planet earth.

4.5. Solid refinery waste

4.5.1 Introduction

The world consumes about 80 million barrels of crude oil[15] per day. It is generally held that the refining capacity of the world is somewhat larger, that is, that the petroleum industry internationally is over-capitalised with refineries[16]. There are a number of factors relevant to this. For example, Japan is very heavily capitalised with refineries, and the entire refining capability of that country is directed at imported oil. As pointed out in an earlier chapter, Vietnam has large amounts of crude oil but only one refinery which came into operation in 2009. It was only about two years before this is being written that the first new refinery in the US since 1976 came into being and even that is intended to receive oil from Mexico! World oil production in 1976 was 57 million barrels per day, and until recently the US was able to accommodate the increases by expansion of existing refineries. If refining is on a huge scale so is the production of refinery waste. Thermal processing of such wastes is the topic of this section.

4.5.2 Refinery sludge

This comprises compounds of about $C_{15\rightarrow30}$ taking in therefore asphaltenes. These are the compounds which in upstream operations with crude oil can cause difficulties with flow in pipes by forming a solid matrix within the oil. This happens if the temperature goes below the pour point. Compounds in the $C_{15\rightarrow30}$ range form a sludge which accumulates at the bottom of storage tanks. It requires disposal and if any saleable hydrocarbons can be made from it so much the better. The Chevron Refinery in Richmond CA salvages about a million barrels a year of useable product from such waste [28] by processes including cracking and fractionation. Otherwise, incineration with return on the heat might be possible. Further examples of such treatment of refinery sludge are given in the table below, which is followed by comments.

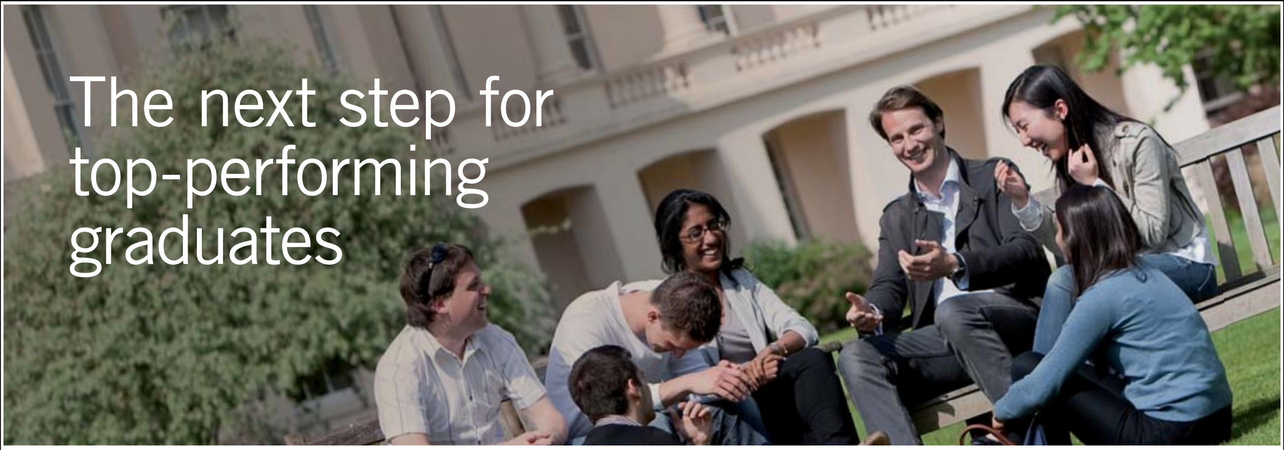
Reference	Details
[29]	Sludge from a refinery in India. The lighter part distilled off and found to be suitable for blending with diesel. Indifferent results when the heavier part was processed to make a hard bitumen.
[30]	Fluidised bed combustion of refinery sludge, also in India. Some samples of the sludge high in moisture through having stood for a long time. This necessitated mixing of different sludges before admittance to the bed.
[31]	Co-firing of refinery sludge, produced from tank cleaning, with coal-water slurry in a fluidised bed. The sludge the primary fuel – see comments below.
[32]	‘Matrix Thermal Systems’ (MTS): refinery residue mixed with a non-hazardous substance such as soil and then irradiated with i.r. to produce a ‘cake’ which can legally be taken to a landfill.

The sludge in reference [29] had accumulated over the previous 20 or more years. The lighter material from it deemed to be a suitable blendstock for diesel had a calculated cetane *index* – not the same as the measured cetane *number* but hopefully a good approximation to it – of 45 which is a very reasonable value. The fluidised bed combustion of refinery sludge was affected by water having entered the sludge as noted in the table. The highest 'as received' calorific value of the sludges was 36 MJ kg^{-1}, indicating about 15% water. The work in [30] was on a pilot scale using 30 to 50 kg per hour of the sludge. On the basis of the results it is stated that the plant in full scale will take about 2 tonnes of sludge per hour. Using the calorific value for the sludge given above, the heat release rate will be:

$$36 \times 10^{6}\ \mathrm{J\ kg^{-1}} \times 2000\ \mathrm{kg\ hour^{-1}}/3600\ \mathrm{s\ hour^{-1}} = 20\mathrm{MW}$$

It was shown in section 4.3.1 of this text that the raising of 1 kg of saturated steam at 1 bar from liquid water at 25°C requires 2.6 MJ. On this basis the fluidised bed combustor under consideration could raise:

$$(20\ \mathrm{MJ\ s^{-1}}/2.6\ \mathrm{MJ\ kg^{-1}}) \approx 7\ \mathrm{kg\ s^{-1}} \text{ or } \approx 600 \text{ tonne per day of saturated steam at 1 bar.}$$



Even at a large refinery 600 tonne per day would be a very significant proportion of the steam requirement. Of course, the figure is for saturated steam at 1 bar and steam at a refinery might be superheated; any diverted to electricity generation almost certainly will be. Moreover, the refinery sludge will not necessarily be available around the clock. It is difficult to see why, if that were so, low-value heavy material from the refining residue could not be substituted. The point being made is that refinery sludge as fuel could make a significant contribution to the steam requirements of a refinery.

The matter of energy-return-on-energy-invested (EROEI) of biomass fuels was raised previously in this book. A rule of thumb is that the EROEI of a gasoline is that for the crude oil from which it was obtained divided by about 1.3. The difference is due not only to fractionation but to technologies such as fluid catalytic cracking (FCC). In the UK sector of the North Sea at the present time a value of about 6 for the EROEI of a crude oil is typical, giving a value of about 4.5 for any gasoline made from it. Skilled and judicious energy auditing at a refinery might make it possible to raise that to about 5 by use of refinery sludge in steam raising. Simply to burn the sludge with no return on the heat will incur carbon credits, making it under those circumstances a ‘fuel of negative financial value’.

The application in the third row of the table look at first sight like one of those enterprises where ‘everybody wins’. The primary fuel is refinery sludge and the benefits accruing from fuel use of that have already been described. The secondary fuel is coal-water slurry. This is a way of utilising coal fines, which otherwise are an extreme dust explosion hazard. A stable slurry can be formed from water and coal particles of median diameter ≈ 30 μm in the correct proportions. Such a slurry will flow like a heavy fuel oil[17].

In Europe and elsewhere refinery sludge is classified as a hazardous waste and direct landfill disposal is precluded. The technology described in the final row of the table involves blending with soil or other harmless substance to dilute the sludge to a degree where it can be taken to a landfill. This involves infra-red treatment to consolidate the mixture of sludge and ‘diluent’ into moulded units of regular shape which can conveniently be handled and transported to a landfill.

4.6 Concluding remarks

All of the wastes discussed so far are capable of processing by pyrolysis or by gasification. The next chapter will give an introduction to pyrolysis and gasification, and their application to waste management will follow. Liquid hydrocarbon waste has a chapter to itself later in the book.

4.7 References

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5. Principles of Pyrolysis and Gasification

5.1 Introduction

In a basic chemistry textbook pyrolysis would be likely to be defined as decomposition by application of heat, or in similar words to those. Some inorganic compounds can be pyrolysed, but in the context of waste management it is of course organics which are of interest.

Pyrolysis and gasification as technologies were developed for application to coal, the former in the late eighteenth century and the latter in the early nineteenth. There is a degree of overlap of meaning between pyrolysis and gasification. When a coal is pyrolysed – ‘carbonised’ would be a more common choice of word in the coal industry – there are three classes of product: solid, liquid and gas, collectively referred to as pyrolysate. Since gas is amongst the products, pyrolysis of coal could be, and frequently is, described as ‘partial gasification’. By contrast when air and/or steam is passed through a bed of coal all of the organic content becomes gas and this is ‘total gasification’. Temperatures of coal carbonisation will be in the range 500 to 1000^{o}C.

5.2 Heat balance in pyrolysis

The process of pyrolysis of an organic material can be represented in general terms as shown in the shaded area below.

$$\text{Starting material} \xrightarrow{\text{heat}} \text{solid, liquid and gaseous products.}$$

Continuing with coal as the starting material but bearing in mind that the principles apply equally to other organics such as MSW and cellulosics, all three classes of pyrolysate will be combustible and have fuel potential. The solid from coal pyrolysis is either coke or char: the difference is in the mechanical strength and degree of swelling on carbonisation and chemically each approximates to pure carbon. The liquid part contains tars and oils[18]. These will comprise hydrocarbon liquids and, depending on the oxygen content of the starting material, oxygenated hydrocarbons. A low-temperature (≈ 100^{o}C) pyrolysis product of wood is methanol, which is why ‘wood alcohol’ is one synonym for methanol. The tar from a bituminous coal will contain little oxygen, that from a low-rank coal (lignite) an appreciable quantity.

Gaseous pyrolysate will be flammable by reason of hydrogen, carbon monoxide and possibly methane within it. There might however be non-flammable components which will act as a diluents, notably carbon dioxide. One would expect very little carbon dioxide from the pyrolysis of a bituminous coal but significant amounts from pyrolysis of materials themselves having a high oxygen content.

There is no reason at all why the total heat releasable by the combined pyrolysis products should equal that releasable by the starting material. That is because some of the heat applied in pyrolysis goes into producing compounds or higher enthalpy than the starting material which will therefore release more heat when burnt to carbon dioxide and water. In the shaded area below is a simplified explanatory diagram.

H_2O and CO_2 in proportions depending on the C:H ratio in the new compound before burning, enthalpy h_3

↑ *combustion*

New compound formed by pyrolysis, enthalpy $h_1 + \Delta h$

↑ *pyrolysis, enthalpy gain* Δh

Compound or structure in the starting material, enthalpy h_1

↓ *combustion*

H_2O and CO_2 in proportions depending on the C:H ratio in the original compound before burning, enthalpy h_2

When the compound or structure in the starting material is burnt the enthalpy change is:

$$h_1 - h_2$$

When the thermally modified compound or structure is burnt the enthalpy change is:

$$(h_1 + \Delta h) - h_3$$

Gaseous pyrolysate is soon removed from the hot pyrolysis zone and will not undergo the further reactions schematised above. At least for coals (which are the focus of the discussion at present) little hydrogen is released on pyrolysis as molecular hydrogen H_2. The product of pyrolysis in response to supply h_2 of enthalpy will therefore have a similar C:H ratio to the original structure and yield on burning a product of similar proportions CO_2 and H_2O. Hence the difference between h_2 and h_3 is small and if it is neglected and the enthalpy is given the single symbol h_f we have:

enthalpy change for combustion of the initial compound or structure = $h_1 - h_f$
and:
enthalpy change for combustion of the compound or structure modified by pyrolysis = $(h_1 + \Delta h) - h_f$

Clearly the second of these is the larger. What is explained here for a single 'compound or structure' will of course apply to many such in pyrolysis of coal, MSW or whatever. So when the combined pyrolysis products have greater potential for heat release than the starting material the difference has been taken from the heat applied during pyrolysis: it is as simple as that!

5.3 Reactions taking place during total gasification

These include:

$$C + 0.5O_2 \rightarrow CO$$

which gives a flammable gas as product. More commonly (in fact just about always) the oxygen is atmospheric, therefore the equation should really be written:

$$C + 0.5O_2\ (+\ 1.88\ N_2) \rightarrow CO\ (+\ 1.88\ N_2)$$

and the effect of the nitrogen is of course to lower the calorific value. The above gas has composition molar or volume basis:

$$CO: 1/2.88 = 35\%\ N_2: 1.88/2.88 = 65\%$$

and is known as Siemens gas, the simplest form of producer gas. Carbon monoxide has a molar heat of combustion [1] of 282 kJ mol^{-1} so, having regard to the fact that 1 m^3 of any gas or gas mixture at 1 bar and 25^{o}C contains 40 moles, the calorific value of the Siemens gas is:

$$40 \times 0.35 \times 0.282\ \text{MJ m}^{-3} = 4\ \text{MJ m}^{-3}$$

Another reaction of importance in gasification is:

$$C + H_2O \rightarrow CO + H_2$$

The above gas for fuel use is called blue water gas (on the basis of the colour of the flame) and has a calorific value of 11 MJ m^{-3}. Such a gas can however be used to make such compounds such as methanol in which case it is known as a synthesis gas. Before cracking technologies for oil products were developed in the early 20th Century synthesis gas was the primary means of organic chemical manufacture. In today's world there is much production of liquid fuels by this means. Production of synthesis gas is a classical technology as we have seen, and the novel content of any current application is often the catalysis by means of which the desired end product, which might be gasoline, is obtained.

A coal gasifier is classified on a MW$_{th}$ basis, that is:

heat which the gas can release on burning/time required to make the gas

and this will be examined against the chemistry given above. Let us suppose that an equimolar mixture of CO and H_2, such as is shown in one of the equations above, is produced from coal waste at a rate of 10^6 m^3 per day. The calorific value of a binary mixture of CO and H_2 in any proportions is 12 MJ m^{-3} to the nearest whole number. The rating of the gasifier in MW$_{th}$ is then:

$$12\ \text{MJ m}^{-3} \times 10^6\ \text{m}^3\text{day}^{-1}/(24 \times 3600)\ \text{s day}^{-1} = 140\ \text{MW}_{th}$$

The time in the formulation refers of course to gasification, so the gasifier rating in MW$_{th}$ must not be equated to the heat-release rate of the manufactured gas fuel after ignition in air.

5.4 The role pyrolysis in combustion

Clearly, if it is intended to pyrolyse a substance the atmosphere must be inert so as to preclude combustion. However, when a substance such as MSW, wood waste or TDF is burnt there will be overlapping combustion and pyrolysis. Heat released at the early stages of combustion feeds back to unburnt material and stimulates pyrolysis. Tars and gases are thus released into the flame and burn there. Pyrolysis in combustion will not be total, so some of the material will burn 'unpyrolysed'. The extent of pyrolysis in combustion depends *inter alia* on heating rate.

The overall process is:

$$\text{waste substance} + \text{air} \rightarrow \text{combustion products}$$

and the enthalpy change is, by the First Law of Thermodynamics, independent of the path[19]. How much fuel burns as pyrolysis product or as 'unpyrolysed' material does not therefore affect the heat of reaction.

5.5 Plasma gasification

An electric plasma results when a normally non-conducting medium such as air bears a current. Temperatures of the plasma are in the range 3000 to 10000K, very much higher than those obtainable in combustion processes. Applications are many and include welding and steel making. Plasma gasification of waste [2] consists heating a carrier gas which enters the waste and breaks it down. The product gas is of moderate calorific value (4 to 5 MJ m^{-3}) and suitable for fuel application and the slag will often have a potential use. Examples of plasma gasification of wastes will be given in a subsequent chapter.

5.6 Concluding remarks

This chapter, whilst concerned with ‘principles’, has focused on coal and appropriately coal waste featured in the calculation immediately above. The gasification of coal waste is of immense importance at the present time in Pennsylvania where piles of such waste having been in existence for a century or more are being dismantled and the coal substance gasified. The sites previously occupied by the coal waste piles are then landscaped and this is to the obvious benefit of residents.

Pyrolysis a.k.a. partial gasification has also been explained in outline, and further comments on this are needed before reader proceeds to the later chapters. We have seen that pyrolysis of any organic waste results in solid, liquid and gaseous products. Each has fuel potential, and in a commercial pyrolysis process much will depend on the suitability of the respective products for fuel use. Can the liquid be used as a fuel, or blended with a conventional fuel, in any widely used combustion appliance? Can the gas be used to supplement or extend natural gas without modification to burners? Is the solid sufficiently strong mechanically to be used as a metallurgical reductant in place of coke? Many more such questions have to be addressed when pyrolysis of a waste is undertaken on an industrial scale, and the feasibility depends on the nature and saleability of the three classes of product. There is however one point of major importance: if the material being pyrolysed is carbon-neutral so are its pyrolysis products[20]. This gives them an intrinsic advantage over their counterparts from coal carbonisation and makes further processing more viable. If for example the liquid component from pyrolysis requires hydrogenation for fuel use the cost of that might well be more than offset by carbon credits generated if the liquid so hydrogenated is used in place of a petroleum product. It is only since about the time of the Kyoto Protocol that substitution of unconventional fuels for conventional ones on the basis of carbon credits accruing has become prevalent and for this reason production of fuels from waste materials themselves carbon-neutral is a growth industry.

5.7 References

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[2] http://www.safewasteandpower.com/process_plasma-gasification.html

6. Examples of Waste Pyrolysis

6.1 Biomass

When wood decomposes it releases a miscellany of simple organic compounds. Many centuries ago, perhaps even in the pre-Christian era, the breakdown products of wood found application, for example as what later came to be called antiseptics. It is sometimes asserted that this is the oldest example of ‘applied chemistry’, ‘chemical technology’ or whatever. The gist of the previous chapter was such that the essentials of biomass pyrolysis were brought out. At the present time there is major interest in co-pyrolysis of biomass with substances including plastics. In this chapter a discussion of such co-pyrolysis will follow coverage of pyrolysis of two very important types of waste: MSW and plastic waste.

6.2 Municipal solid waste

MSW combustion, in raw and pelletised form, was the subject of three previous chapters. Discussion of its pyrolysis was deferred until background on the pyrolytic processes generally had been given. There has been and is much interest in the pyrolysis of MSW and that will be the subject of this section.

Attempts to make useful products from pyrolysis of MSW are by no means new. An account of pyrolysis on a trial basis of ‘municipal garbage’ features in a monograph from 35 years ago [1], nor was that the first such investigation to be reported. The table below gives selected examples of pyrolysis of MSW. The examples in the table range from laboratory scale to full, commercially operating scale. Comments follow the table.

Reference	**Details**
[1]	Pyrolysis temperatures in the range 500 to 900°C. Per tonne of raw MSW, up to 200 kg of char, up to 15 litres of oil and up to 500 m^3 of flammable gas.
[2]	Pyrolysis of laboratory size samples of rubber, paper, wood chips, ‘fabric’, foodstuff and polyethylene, simulating the separate components of MSW. Respective reactivities to decomposition investigated by thermal analysis.
[3]	Pyrolysis of the paper component only of MSW at 450°C, directed at oil as the primary product.
[4]	MSW pyrolysis with combustion of the products for generation of electricity most of which is sold to the grid.
[5]	Pyrolysis of Tetra Pak [6] products. A considerable amount of wax in the pyrolysate.
[7]	Laboratory study of the pyrolysis of RDF pellets. Pyrolysis temperatures up to 700°C.
[8]	Funabashi City, Japan (part of Greater Tokyo), pyrolysis of MSW in a quantity of 450 tonne per day. Pyrolysis products used as fuel in electricity generation.
[9]	Laboratory-scale pyrolysis of paper at temperatures up to ≈ 700°C. Calorific value of the paper 12.5 MJ kg^{-1} dry basis.
[10]	RDF in the form of fluff pyrolysed in small (24g) laboratory samples at temperatures up to 1000°C. Significant amounts of methane in the products.
[11]	Epoxy resin, as a component of MSW, studied for pyrolysis kinetics.

Reference [1] states that the gas yielded in the pyrolysis was comparable to town’s gas. ‘Town’s gas’ is a term having largely gone into obsolescence since reference [1] was published, but it means either gas from partial gasification of coal or gas from total gasification supplemented with some cracked hydrocarbon vapour (‘carburetted water gas’). Each has a calorific value of 20 MJ m^{-3}. The fact that the gas in [1] had such a high calorific value must mean that considerable amounts of methane were present additionally to carbon monoxide and hydrogen, possibly also some ethane or ethylene. In the work summarised in the second row of the table the components showed the trend expressed in the shaded area below:

rubber
foodstuff
wood chips, ‘fabric’
polyethylene

ease of breakdown
↓

The work in reference [3] originates in Bangladesh, and its ultimate aim was to examine liquid pyrolysis products of paper waste for possible use with or in place of petroleum products in particular diesel. Yields of liquid of about 50% were obtained but with the very low calorific value of 13 MJ kg^{-1}. This suggests that de-watering will be necessary before fuel use becomes viable. The water in the fuel might well have been not from moisture in the feedstock but product water resulting from breakdown of the cellulose. In the plant described in the following row, which originates in the Netherlands, steam is raised from combustion of the pyrolysis products and used to raise steam for power generation as explained.

Tetra Pak (row 5 of the table) products originate in Sweden and comprise a variety of food packaging materials adapted for particular applications and circumstances, for example long-term storage in a refrigerator. Low-density polyethylene, a common choice of material for the coating of paper, is present at about 20% in Tetra Pak products and it was found that on pyrolysis this gave a wax product. Polyethylene wax is of course a saleable substance although, of course, specifications apply according to the intended use. At pyrolysis temperatures of 600^{o}C or higher the yield of wax from the polyethylene content of the Tetra Pak is quantitative.

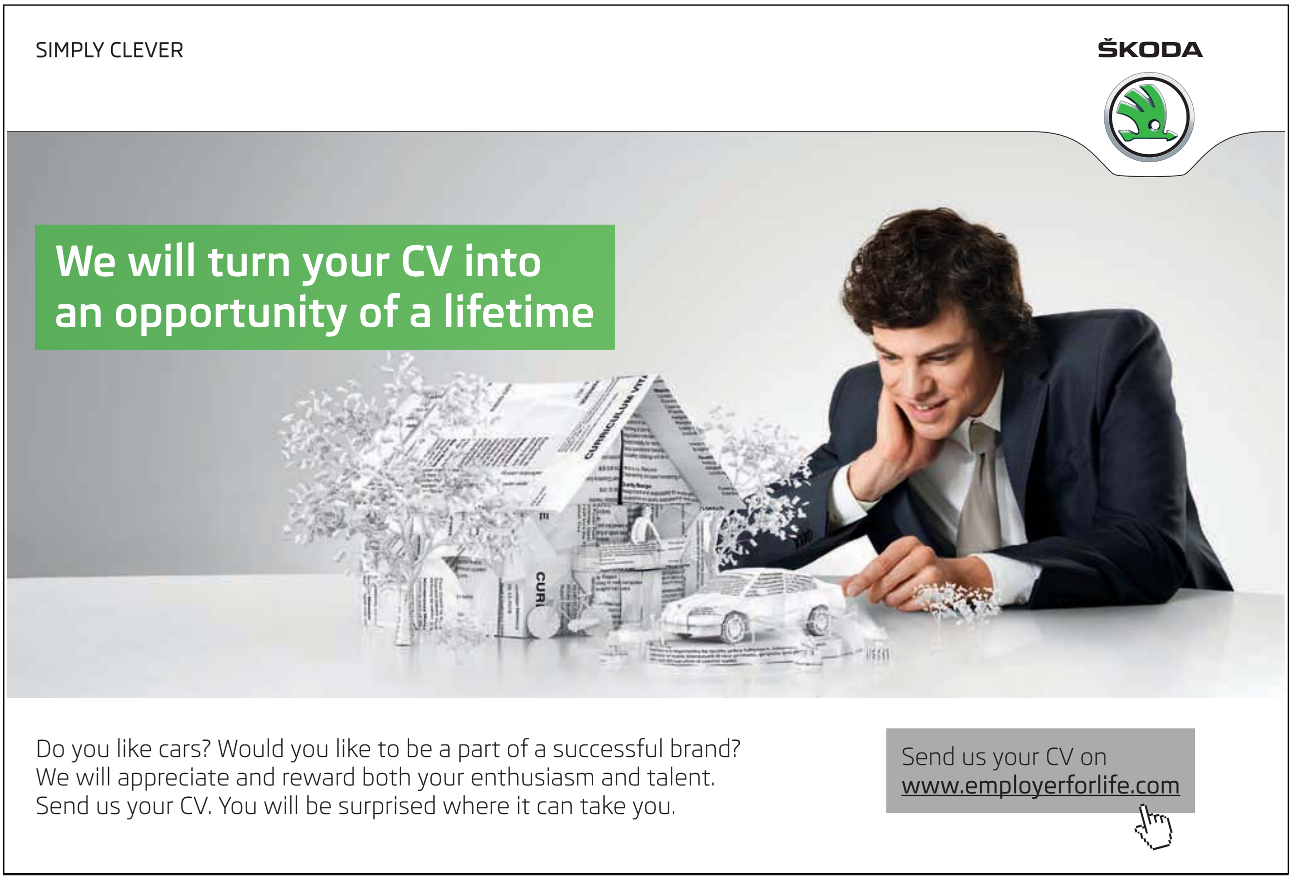
In row six of the table pyrolysis of MSW in pelletised form, that is of RDF, features. The pellets were as low as 4% in moisture with the correspondingly high calorific value of 18 MJ kg^{-1}. At a pyrolysis temperature of 700^{o}C the gaseous product was about 25% carbon monoxide, 1% hydrogen and 5% methane, balance carbon dioxide. From calculations of the type which have been performed earlier in this book it is easily shown that such a gas would have a calorific value of just under 5 MJ m^{-3}. At somewhat lower pyrolysis temperatures, up to 3% of C_2 gases – ethane and ethylene – were formed also C_3 and C_4 gases in yields of about 1%. It is possible that these are not primary pyrolysis products but cracking products of the liquid pyrolysate. The liquids in fact had a calorific value of 35 MJ kg^{-1}, a surprisingly high value auguring well for subsequent fuel use. The char residue for pyrolysis at 700^{o}C had a BET surface area of over 200 m^{2}g^{-1}. For a carbon not ‘activated’ either by steam or with a chemical agent such as phosphoric acid this is a large surface area indicating promise of the product even without such activation as an adsorbent. Rows three and eight of the table are each concerned with studies of the paper component only of MSW, respectively in Bangladesh and in Taiwan. In row eight the calorific value of the paper in the work described has been noted because it is significantly below that of pure cellulose. This indicates the presence of an inorganic filler such as barium sulphate, a point which the authors of [9] have missed. That this could catalyse or in some other way influence pyrolysis behaviour is of course quite possible. At the highest of the pyrolysis temperatures in this study mass loss was about 75% or, equivalently, solid residue yield was about 25%. In some of the experiments levoglucosan $C_6H_{10}O_5$ was identified in the pyrolysis products.

Epoxy compounds are ubiquitous and that some will find their way into the ‘city waste’ is inevitable. The work in the final row of the table is concerned with decomposition of an epoxy resin and Arrhenius parameters are determined. As would be expected these differ with extent of decomposition, and up to a fractional extent of 0.7 the value is in the range 150 to 170 kJ mol^{-1}. This is a high value representing a pyrolysis rate very sensitive to temperature. The value of the pre-exponential factor ‘A’ of 10^{13} s^{-1} is also remarkably high for pyrolysis of an organic substance.

This section has been concerned with pyrolysis of MSW or particular components thereof and it will be followed by a discussion of pyrolysis of plastic wastes. Quite often MSW and plastic are blended for pyrolysis, and this will receive its due coverage at a later stage of the chapter.

6.3 Plastic waste

Polymer substances are of course made from petrochemicals and one expects abundant yields of hydrocarbons when they undergo pyrolysis. The approach taken in the previous section for MSW will be followed here for plastic waste: tabular presentation of information backed up with references and followed by comments.



Reference	Details
[12]	Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) pyrolysed in a laboratory-scale fluidised bed reactor at temperatures up to 700°C. When all of the plastics were pyrolysed together gaseous products included hydrogen, methane, ethane, ethene, propane, propene, butane and butene. Also some carbon monoxide. At the highest temperatures used an 88% gas yield. Wax/oil yields of up to 55% at the lower pyrolysis temperatures.
[13]	Chennai, India. Plastics excluding PVC and PS pyrolysed to give a preponderance of liquid product*.
[15]	Plastic waste containing PE, PP, PS, PVC, PET and acrylonitrile butyl styrene (ABS) pyrolysed in 100 g samples. Liquid pyrolysate with calorific value up to 41 MJ kg^{-1} containing compounds in the range C_6 to C_{21}. Significant quantities of hydrocarbons in the gasoline carbon number range.
[16]	Pyrolysis of shredded plastic waste followed by cracking of the pyrolysate. Data examined for EROEI below.
[17]	PE, PS and PP pyrolysed at temperatures up to 750°C with the intention of making gasoline. Yields of oil from PE and PP 40 to 50%. Yield from PS 25% plus major amounts of styrene monomer.
[18]	Kinetic analysis of pyrolysis of mixtures of PE and PS.
[19]	Pyrolysis of PVC in 10g quantities at temperatures up to 1100°C.
[20]	Pyrolysis of PVC.

*Abbreviations for the respective polymers given in row 1 retained.

In reference [12] (row one) the plastics identified were pyrolysed both individually and all together. In the latter case the yield of gas at about 700°C was remarkably high, and the gas would have had a calorific value on a volume basis higher than that of natural gas let alone that of the producer gas. The potential for fuel use of the gas is clear but there are important questions to be addressed first. Containing several hydrocarbons in the $C_{2\rightarrow4}$ range, the gas would not be suitable for use on a burner designed and adjusted for natural gas. Indeed, serious accidents have resulted when LPG (C_3 and/or C_4) has been substituted for natural gas on a burner designed expressly for the latter. The reason is that methane, being C_1, is the least reactive alkane. Ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) have higher reactivities than methane and therefore higher flame speeds. The expected result when a mixture of these is substituted in ignorance for natural gas is burner flashback. A high-BTU gas produced by pyrolysis becomes a less attractive resource if its use involves burner adjustment or even replacement. Possibly such a gas, if available in small but steady and reliable supply, would on a burner designed and tested for the gas be suitable for use in an application such as flame cutting in which usage is intermittent and amounts of fuel gas used are not huge.

The plant at Chennai (second row) was made by Polymer Energy^{TM} in the US, which has a number of installations in the East including one in Thailand [14]. It produces 750 to 800 litres of oil per tonne of waste processed and this is seen as having refining potential. It is interesting to note that PS is not accepted at the plant, and the reason on reflection is fairly obvious. The empirical formula of styrene monomer is CH, and the low hydrogen-to-carbon ratio will make for a low extent of pyrolysis to gaseous products and large amounts of char and/or organic sludge. As well as not being the desired product, these adhere to surfaces within the reactor and necessitate more frequent cleaning than would otherwise be the case. The empirical formula of ethylene monomer is CH_2, and the plant at Chennai accepts polyethylene 'within certain limits' [13]. PP – monomer empirical formula C_3H_8 or in effect $CH_{2.7}$ – is accepted unconditionally at the plant.

To the information in row three will be added the following. The gaseous pyrolysate has calorific values of 47 MJ m^{-3} indicating a preponderance of C_{2+} gases. The solid residue the organic composition of which will approximate to pure carbon has quite low calorific values, only up to 17 MJ kg^{-1}. This is of course due to the presence of such materials as glass and these residues would not be suitable for direct combustion because of the quantity and nature of the ash which the combustion would generate. Gasification would be possible but here again the high ash would work against viability. If the char were steam activated or chemically activated to make an adsorbent it might function well enough as such, but a common eventual fate of adsorbents is incineration so even this application is precluded by the ash and the solid is the least attractive of the three classes of pyrolysate from the study in [15].

In reference [16], pyrolysis followed by cracking of the product, pyrolysis gas is burnt to provide heat for cracking and this need not feature in an EROEI calculation which, it must be remembered, is in no sense an energy balance. It is stated in [16] that 8 m^3 per day of liquid in the gasoline and diesel boiling ranges is produced and that heat for the pyrolysis is provided electrically with a daily consumption of 500 kW hour. These data are examined in the boxed area below.

500 kW hour = 500 × 10^3 × 3600 J ≈ 2 GJ. 8 m^3 of the liquid ≈ 7000 kg
Assigning a value of 40 MJ kg^{-1} to the calorific value, this quantity of the liquid is capable of releasing on burning ≈ 300 GJ of heat
EROEI = 300/2 = 150

The EROEI calculated would exceed that for any crude oil in this early 21st Century, but 150 would in fact have been a typical value about 60 years ago when offshore oil and gas production were just beginning in the Gulf of Mexico using wells which by today's standards were very shallow. So there is no reason why the EROEI calculated above cannot be at least cautiously accepted and it augurs well for the production of liquid fuels by the treatment of plastic waste described in [16]. Of course, there would be quality issues to be addressed were the liquids to find automotive use. The same would be so were the mixture of pyrolysis oils and styrene monomer referred to in the next row to be used as fuel for a spark ignition engine. The styrene would enhance the octane number, but whether such a mixture would be suitable for use in viscosity and vapour pressure terms would need close attention.

The kinetic modelling work referred to in the antepenultimate row of the table led to the conclusions that the most influential factors in determining the distribution of products are temperature and weight ratio of the two polymers co-pyrolysed. If oil is the desired product a temperature of 600°C is most suitable. Interestingly, the analysis predicts that other things being equal a PE-PS mixture decomposes to oil more rapidly than PE alone. PVC pyrolysis features in the next row, and it is widely known that this leads to hydrogen chloride and char in a process known as 'dehydrochlorination'. In [19] it was observed that this process began at 250°C and that at 350°C the PVC had lost 99.5% of its chlorine content. This means negligible chlorine in the char residue, which was found to have a calorific value as high as 38 MJ kg^{-1}. This indicates significant hydrogen in the char, and a simple calculation is possible to show this. Vinyl chloride monomer having undergone 'dehydrochlorination' consists of a fragment $C_2 H_2$ having:

(2/26) × 100% = 8% hydrogen to the nearest whole number.

At 350°C the char remaining after hydrogen chloride release will not dehydrogenate to a major extent, though it will at the higher temperatures used in the work under discussion. A value of 8% is an unusually high one for a char, and the calorific value of the char is higher than that of elemental carbon. This is due to the high hydrogen content of the char. Reference [20] (final row of the table), also concerned with PVC pyrolysis, confirms that beyond the limit of dehydrochlorination at about 300°C there is hydrocarbon gas production, and this will of course reduce the hydrogen content of the residue to a value more typical of a char.

It is fairly clear that some control over pyrolysis product nature and distribution is achievable by adjustment of reacting conditions. Similarly co-pyrolysis – that is, pyrolysis of two substances as a mixture - can be used to give a good yield of desired product and there might be other good reasons for co-pyrolysis including concurrent treatment of municipal and trade waste. In the first part of this chapter biomass pyrolysis was discussed with special emphasis on co-pyrolysis with some other type of waste. Consequently some examples of co-pyrolysis will be studied in the next section.

6.4 Co-pyrolysis

One obvious point is that to co-pyrolyse biomass with plastic in some degree mitigates the non carbon neutrality of the latter, giving any pyrolysate product for subsequent fuel use a degree of carbon neutrality which can be estimated and factored into carbon accounting. This is analogous to coal-biomass co-firing in combustion. A hot-off-the-press report [21] originating from Romania describes co-pyrolysis of PE, PP and PS with a form of biomass locally available in abundance, namely pine cones (Pc). These were co-pyrolysed at 500°C. Pc and PE in a weight ratio of 1:1 gave a product distribution gas 15.9%, liquids (total, aqueous + organic) 47.5% and char 36.6% Results were not widely different with Pc and PP; however, the trend noted above whereby PS gives on pyrolysis very limited gas was found in [21], and Pc and PS in equal quantities gave only 8.8% of gas. There was detailed analysis by GC-MS of products and the compounds in the aqueous phase were diverse. With Pc and either PE or PP or PS the aqueous pyrolysate had up to 10% of carboxylic acids up to C_3, acetic acid being the most prevalent. With the various Pc plastic mixtures studied the tar/oil component of the products contained compounds up to about C_{26} with calorific values sometimes as high as 46 MJ kg^{-1}. Chars had calorific values up to about 35 MJ kg^{-1}; a bituminous coal with this calorific value would be expected to attract a good price!

Co-pyrolysis of biomass with coal is also of increasing importance, and here again a degree of carbon neutrality is introduced by inclusion of the biomass. In a fairly recent experimental study [22] of coal-biomass co-pyrolysis the coal was a low-rank one, actually a lignite originating in China given in [22] the abbreviation DY. This was co-pyrolysed with legume straw (LS) at temperatures in the range 500 to 700°C. Across the temperature range an increase in the LS:DY ratio led to a decrease in char yield as would be expected and an increase in gas yield; liquid yield was not very strongly affected. A high LS:DY ratio raised oxide of carbon yields in the gaseous pyrolysate and had the same effect on hydrogen yields. If fuel utilisation of the gas was intended, carbon *mon*oxide and hydrogen would be the most desired products. Methane, having a much higher calorific value molar basis than either hydrogen or carbon monoxide, is a significant bonus in such a pyrolysate gas even at low levels. It occurred at about 2% level in the work under discussion.

Oil is of course obtained from shale by pyrolysis of the kerogen within the shale leading, probably after desulphurisation and hydrogenation, to syncrude. The idea of including plastic waste with shale for pyrolysis is an interesting one and has been examined in work including that described in [23]. In this work shales from two sources were pyrolysed with and without low-density polyethylene (LDPE) at temperatures up to 500°C and effects of the LDPE assessed. Not only amounts of products but also their distribution was affected by the LDPE, and the yields of products is particular carbon number ranges was controllable by means of the dual factors of temperature and kerogen:LPDE ratio. Reference [23] was published in 1998 and a question which has crossed the present author's mind would almost certainly not have been raised in 1998. Wherever there are attempts to make oil from shale the EROEI is of paramount importance. Is there potential to raise the EROEI by co-pyrolysis of the kerogen with plastic? Oil from shale usually operates on a slender EROEI and is therefore vulnerable if there is a downward movement of conventional oil prices. We might expect to see more of the type of work described in [23] as efforts are intensified to produce oil from shale, for example in parts of the US including Colorado.

6.5 Concluding remarks

The scope for production of organic chemicals from pyrolysis of waste is very wide indeed. Gaseous pyrolysate can always be used as a fuel gas or as a synthesis gas. Liquid pyrolysate can always be used as a liquid fuel. Solid residue can always be used as a solid fuel or to make products such as adsorbent carbons. The challenge is in making use of the pyrolysis products viable under circumstances such that they are produced 'here and there' without any national (let alone international) network or distribution structure and are in competition with conventional fuels with extensive capitalisation in distribution infrastructure.

6.6 References

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7. Examples of Gasification of Wastes

7.1 Raw MSW

Against a background of the principles of gasification given Chapter 5 selected examples of gasification of waste will be discussed, starting with MSW. These are in the table below which is accompanied by comments.

Reference	Details
[1]	Averøy, Norway. Annual processing of ≈ 16000 tonnes of MSW in addition to commercial wastes. Gaseous fuel obtained used to provide steam for a nearby factory.
[1]	Stavanger, Norway. A waste gasification plant capable of treating 40,000 tonnes per annum of MSW. Power and hot water from the gas produced.
[1], [3]	Isle of Wight, England. Electricity at 2.3 MW from local MSW after gasification.
[4]	MSW compacted to a bulk density of about 1000 kg m^{-3}. Gasification to give a product of calorific value 9 MJ m^{-3}.
[5]	Plant under construction in Nevada for synthesis gas from MSW for subsequent conversion to ethanol for fuel use. Expected production 10.5 million (US) gallons per year of ethanol from 90000 (US) tons of waste.
[6]	Plant under construction in Edmonton, Canada to make 9.5 million gallons of ethanol annually from 110000 US tons of waste.
[7]	S. Korea. A three ton per day pilot gasifier yielding a gas roughly one third each in CO, CO_2 and H_2.

The plants at Averøy and at Stavanger (rows one and two) were manufactured and installed by Energos, who have plant in other countries including the UK. The information on the Stavanger plant will be used in the approximate calculations below.

MSW varies widely in composition, but the following figures can be seen as being typical for raw MSW:

Moisture 25%

Non-combustibles 25%

Carbon 20%

Hydrogen 3%

Accordingly 1 kg of raw MSW will contain 200 g of carbon and 30 g of hydrogen. Other elemental figures need not concern us in this calculation.

If the MSW is gasified with steam and the reaction:

$$C + H_2O \rightarrow CO + H_2$$

goes to completion there will be (200/12) = 16.7 mol each of CO and H_2 from gasification of 1 kg, as well as (30/2) = 15 mol of H_2 from devolatilisation giving a total:

16.7 mol CO and 31.7 mol H_2 capable of releasing on burning:

$$[(16.7 \times 283) + (31.7 \times 286)]\ \text{kJ} = 13.8\ \text{MJ of heat}$$

Now the Stavanger plant under consideration gasifies 40000 tonne per annum, and the heat release rate obtainable from the products can be estimated as:

$$[13.8 \times 10^{6} \times 40000 \times 10^{3}\ \text{J}/(365 \times 24 \times 3600)]\ \text{W} = \underline{17.5\ \text{MW}}$$

If the entire heat was diverted to electricity generation about 6 MW would be yielded, or an annual quantity[21]:

$$6 \times 10^{-3} \times 365 \times 24\ \text{GW hour} = 53\ \text{GW hour}$$

As explained in the table, at present not all of the energy is used to make power, some being used in steam generation for heating. Note also that the gas will make for a much cleaner burn than solid MSW.

The calculation can be taken a little further in the following way:

Total moles of gas from treatment of 1 kg of waste = (16.7 + 31.7) = 48.4

Volume occupied by the gas at 1 bar pressure 288K =

$$48.4 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 288\text{K}/10^{5} \text{ N m}^{-2} = 1.16 \text{ m}^{3}$$

$$\text{Calorific value} = 13.8 \text{ MJ}/1.16 \text{ m}^{3} = 12 \text{ MJ m}^{-3}$$

The gas in reference [4] has a calorific value of 250 BTU per cubic foot, equivalent to

$$250 \text{ BTU} \times 252 \text{ cal BTU}^{-1} \times 4.2 \text{ J cal}^{-1}/0.028 \text{ m}^{3}\text{foot}^{-3} = 9.5 \text{ MJ m}^{-3}$$

somewhat lower than that calculated above. The reason is that carbon monoxide to the exclusion of the dioxide is not quite achieved and the carbon dioxide so formed becomes a diluent.

The examples dealt with so far have produced gas for fuel use: reference [5] (fifth row) by contrast is concerned with use of the gasification product of MSW as a synthesis gas to make ethanol. An approximate mass balance will verify the production figures given in the table. This is in the shaded area below.

10.5×10^{6} US gallons of ethanol equivalent to:

$$= 10.5 \times 10^{6} \times 3.785 \times 10^{-3} \text{ m}^{3} \times 785 \text{ kg m}^{-3} = 31198 \text{ tonne}$$

This requires from the waste:

(31198 × 24/46) tonne carbon =16277 tonne carbon

Using the analysis figures for MSW from the previous page, weight of waste =

(16277/0.2) tonne = 81385 tonne or (81385/0.91) US ton

= 89434 US ton

and the figures in the table have been reproduced exactly.

The figures in the following row for the Edmonton Canada plant correspond very closely to those for the Nevada plant so the above calculation, with its very impressive agreement with the published expected production, applies equally to the Edmonton plant.

7.2 RDF pellets as gasification feedstock

It is clear from the contents of an earlier chapter of this book that by the time MSW has become RDF pellets it has been value-added, and more is expected of it than of raw MSW. The latter might well be of negative financial value: RDF will always be of positive financial value. That for a limited number of applications RDF can replace coal is the reason for its production, and such replacement can apply not only to combustion but to gasification. It was shown in Chapter 5 how producer gas can be made by passing air through a hot bed of coal, and RDF pellets have been substituted for coal in producer gas manufacture, e.g. [7]. Air only, not air/steam, was used in the gasifier described in [7] therefore the gas was also describable as Siemens gas. A calorific value as high as 5.6 MJ m^{-3} was reported for the gas obtained by blowing air only through a bed of RDF, whereas Siemens has from coke as only about 4 MJ m^{-3} as was shown in Chapter 5. Coke has no volatiles, and Siemens gas made from a coal with a moderate volatile content, say a high-volatile bituminous, might be expected to have a somewhat higher calorific value by reason of devolatilised methane. This principle carries through to RDF pellets with their very high volatile content and given their price advantage over coal RDF pellets might on these grounds appear to be a good feedstock for producer gas manufacture. Two further points, one a plus and one a minus, can be made. The plus is that any carbon neutrality of the RDF will carry through to the producer gas. The minus is that since producer gas is made by partial combustion and involves total reaction of the organic component there being no char, the large amounts and corrosive nature of the ash from the pellets might make for difficulties. Producer gas from RDF pellets is also the theme of reference [8] which describes a gasifier taking 200 tonnes per day of RDF to make a gas of 7.4 MJ m^{-3}. Analysis figures for the gas are given and methane is 6.5% molar basis whilst C_{2+} hydrocarbons are as high as 4.9%. Very possibly the higher hydrocarbons originate from tar cracking.

7.3 Co-gasification

Co-gasification might be of one waste substance with another or it might be of a waste substance with a conventional feedstock, commonly coal. Examples of the latter are given in the table below.

Reference	Details
[9]	RDF pellet gasification with lignite and supply of the fuel gas to a steam turbine and to a gas turbine to make electricity. Lignite in a bed-moist state, having a lower calorific value than the RDF pellets.
[10]	Tyre waste and lignite co-gasified in steam and oxygen. Calorific value of gas produce from gasification of lignite alone and that produced by co-gasification of lignite with tyre waste respectively 12.4 and 12.8 MJ m^{-3}.
[11]	Synthesis gas from Colombian coal co-gasified with biomass in a fluidised bed. Temperatures up to ≈ 900°C.
[13]	Co-gasification of coal with biomass to make a gas which is partly carbon neutral. Carbon credits accruing.

Reference [9] (first row of the table) uses a blend of 25% by weight lignite, balance RDF pellets and a third of the electricity is generated at the steam turbine, two thirds at the gas turbine. Production of electricity is a fairly modest 30 MW. The most noteworthy feature of the results in [10] is the high calorific value of the of the gas pyrolysate, up to 40 MJ m^{-3} at the higher end of the pyrolysis temperature range. This is due to a high proportion of C_{2+} alkanes, and analyses were carried out. The density of this gas is given in [10] as 1.22 kg m^{-3}, from which the average molecular weight is:

$$1.22 \text{ kg m}^{-3}/42 \text{ mol m}^{-3} = 0.029 \text{ kg mol}^{-1}$$

which corresponds almost exactly to the value of 0.030 kg mol^{-1} for ethane C_2H_6. Results in the following row for Lurgi gasification of lignite only and of lignite with tyre waste reveal a very marginal improvement with the co-gasification in calorific value terms, and there will of course be some carbon neutrality benefits arising from the natural rubber component of the tyres. Notwithstanding what has been said previously about 'total gasification', it has long been the case that Lurgi gasifiers are operated in such a way as to produce some tar by-product. For example, the Lurgi process was used in Melbourne Australia between 1956 and 1969[22] to make town's gas, and there was considerable interest in the by-product 'Lurgi tars'. In [10] there are significant liquid by-products which have calorific vales of 38 MJ kg^{-1} and kinematic viscosities of 10 to 20 cSt. He or she would be an unimaginative fuel technologist who could not conceive an application for such liquids. Values for their cloud and pour points would have been a helpful addition to the information on them in [10].

This book is not a comprehensive review or critique of the subject area, but nor is it a 'child's guide'. Readers of a book at this level will, when applying the contents, need to have a professionally critical attitude and the capability to distinguish stronger R&D from weaker. Reference [11] (third row of the table) describes the co-gasification of Colombian coal with various forms of biomass. The coal is itself an asset, perhaps Colombia's most important one: she exports about 80 million tonnes of coal per year [12] and that is three times the annual coal production of the UK. One is therefore dismayed to read in [11] that co-gasification of Colombian coal with various forms of biomass including sawdust and coffee husk produces gas having calorific values in the range 1.6 to 4.2 MJ m^{-3}. A gas of 1.6 MJ m^{-3} could not sustain a flame on a burner; losses of heat and reactive intermediates to the metal burner structure would be too severe for propagation to occur. The value of 4.2 MJ m^{-3} is at the low limit for maintenance of a flame on a suitable burner, most likely one designed for producer gas. But that this should be the product of fluidised bed co-gasification of quality coal with biomass is a disappointing result. The product gas is presumably heavily diluted with nitrogen from air used in the gasification process.

7.4 Scenes of plasma gasification

A very brief description of this process was given in Chapter 5, and this will be backed up by a number of case studies. In reference [14] fuel comprising carpet and textile waste having a measured carbon content of 60% underwent plasma gasification at a rate of 22 kg hour^{-1}. Electricity consumption was in the range 82 to 112 kW. An attempt to examine these figures semi-quantitatively forms the calculation in the shaded area below.

If the primary gasification reaction:

$$C + 0.5O_2 \rightarrow CO$$

is taken to be the sole reaction occurring and it goes to completion, rate of CO production =

$$[(22000 \times 0.6/12)/3600] \text{ mol s}^{-1}$$

$$= 0.3 \text{ mol s}^{-1}$$ capable of releasing on burning:

$$0.3 \times 282 \text{ kW} = 85 \text{ kW}$$

which is at the low end of the range of the power consumption.

The result obtained appears to signify an EROEI of the order of unity, possibly enhanced by carbon credits. The tests in the work under discussion were on a small scale and full assessment of the slag was not possible as there was too little of it. Such evaluation as was possible indicated that it complied with local regulations for 'secondary building materials'. The work in reference [15], originating in China, was also on a small scale and was concerned with plasma gasification of biomass. Biomass feed was at 18 g hour^{-1}. This is an order of magnitude lower than that in [14] and electricity consumption was also lower, in the range 1.6 to 2.0 kW. Gas yielded was in the range of calorific values 4.18 to 4.93 MJ m^{-3}.

The first full-scale plasma gasifier in the US, which will be in Florida, is expected to come into operation in 2011 [16]. The gas will be used to make electricity. It will process 1500 tons of waste per day and after its own very high electricity demand has been met there will remain 60 MW to sell to the grid.

The table below gives details of five plasma gasifiers which are either operational or under development. Comments follow the table.

Reference	Details
[17]	St Lucie, FL. Plasma gasification of up to 3000 tons per day of waste from an existing landfill site. Up to 120 MW of electricity for sale on to customers.
[17]	New Orleans, LA. Plasma gasification of up to 2500 tons per day of waste. Electricity for supply to the grid.
[17]	Istanbul, Turkey. Plasma gasification of 144 tons per day of hazardous waste.
[18]	Yoshii, Japan. Plasma gasification of 24 tonnes per day of raw MSW.
[18], [19]	Utashinai, Japan. Plasma gasification of MSW and Auto Shredder Residue (ASR) at ≈ 170 tonne per day.

The Florida facility (row one) will produce slag which, it has been confirmed, can be used in road construction. The facility at Yoshii (row four) is a small-scale one the electricity production from which is used entirely by a local hotel and leisure complex. ASR (row five) is the non-metallic moiety of destruction of automobiles, containing for example upholstery material, rubber and plastic. At the plant in Utashinai it is fired with coke and there is little if any electricity remaining for sale after the plant’s own requirements have been met. One difficulty is that Utashinai has a low population[23] making waste supply to the plant limited and at times uncertain.

7.5 Concluding remarks

The examples covered in this chapter have been diverse and will hopefully have enabled a reader to understand and interpret reports of gasification of waste. Such reports abound in the current research literature and this signifies ongoing interest and investment.

7.6 References

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8. Hydrocarbon Waste

8.1 Introduction

The technologies discussed previously in this book – incineration, gasification and pyrolysis – have usually been discussed with solid waste as examples. A reader will have concluded for him/herself that they can all be applied to liquid waste. When a solid is incinerated it is the gas and vapour breakdown products which burn: when a liquid is incinerated it is the evaporated liquid which burns. Not only do the same ideas apply but also the same sorts of plant, and fluidised-bed incineration of liquid wastes is quite common. Similarly, plasma gasification has found recent application to waste lubricating oil [1]. It is probably unsound to impose a distinction between solid and liquid incineration given that in either case it is gas or vapour which burns as explained above. In this chapter methods of disposal of waste hydrocarbons will be outlined. Such hydrocarbon will occur at refineries. Heavy fuel oil provides a way of making a marketable product from the heavy residual material, but such a fuel oil is never simply a 'rag bag' of otherwise unwanted hydrocarbons as strict specifications, for example of viscosity and cloud point, apply. Lubricants and hydraulic fluids are amongst the other products which eventually become hydrocarbon waste. Additionally to incineration and the other methods previously discussed in this book, the very important topic of re-refining of hydrocarbon waste will also feature as will cracking.

8.2 Incineration

Hydrocarbon liquids have calorific values of about 40 MJ kg^{-1}. As with other materials for incineration, if some return can be obtained on the heat so much the better. The table below which is followed by comments gives some examples of waste oil burning.

Reference	Details
[2]	Small-scale incineration of used lubricating oil from a power station.
[3]	Portable incinerators for use in Alaska.
[4]	Oil burners in a range of sizes capable of taking from ≈ 5 to ≈ 12 litres per hour of waste oil. Applications have been to waste hydrocarbons including transmission fluid and hydraulic fluid.
[5]	An incinerator for waste oil from oil tankers, performance about 350 kW.
[7]	Mid 1980s, 8000 megatonne of tarry waste from vinyl chloride manufacture destroyed by ocean incineration annually.

The application in the first row of the table is in a remote location in the Middle East requiring self-sufficiency in such operations as oil disposal. Reference [3] gives some performance figures which will be examined below.

The burner in [3] operated in the range 0.33 to 0.92 gallons per hour, and we use the information for the trial at 0.65 gallons per hour ($\approx 7 \times 10^{-4}$ kg s^{-1}). The thermal delivery is then:

$$7 \times 10^{-4}\ \text{kg s}^{-1} \times 40 \times 10^{6}\ \text{J kg}^{-1} = 28\ \text{kW}$$

The authors report 60060 BTU $hour^{-1}$ which becomes:

$$(60060\ \text{BTU hour}^{-1}/3600\ \text{s hour}^{-1}) \times 252\ \text{cal BTU}^{-1} \times 4.2\ \text{J cal}^{-1} \times 10^{-3}\ \text{kW}$$

$$= 17.7\ \text{kW}$$

This is 63% of the calculated value and the author of [3] does report a ‘burner efficiency’ of 66%[24].

The information in [4] (third row of the table) can also be analysed quantitatively and this follows in the shaded area.

The middle-of-the-range burner in [4] takes about 9 litres per hour of fuel, which using a value of say 900 kg m^{-3} for the density equates to:

$$9 \times 10^{-3}\ \text{m}^3 \times 900\ \text{kg m}^{-3}/3600\ \text{s} = 2.3 \times 10^{-3}\ \text{kg s}^{-1}$$

Now the empirical formula of all heavier hydrocarbon liquids approximates to CH_2,

so the figure of 2.3×10^{-3} kg s^{-1} for the fuel supply rate becomes:

$$2.3 \times 10^{-3}\ \text{kg s}^{-1} / 0.014\ \text{kg mol}^{-1} = 0.16\ \text{mol s}^{-1}$$

The combustion stoichiometry is:

$$CH_2 + 1.5O_2\ (+\ 5.64\ N_2) \rightarrow CO_2 + H_2O\ (+\ 5.64\ N_2)$$

and one mole of the waste oil requires 1.5 mole of air or 0.0432 kg for complete burning. Per second the air requirement is then:

$$0.16 \times 1.5\ \text{mol} = 0.24\ \text{mol or } (0.24/42)\ \text{m}^3 = 0.0057\ \text{m}^3 \text{ or } 0.2\ \text{ft}^3$$

Knowledge of the air requirement is important as the burner will not rely on natural fuel-air contacting but will have an air supply by means of a compressor. An excess of air of about 20% will be typical. The thermal delivery will be:

$$2.3 \times 10^{-3}\ \text{kg s}^{-1} \times 40 \times 10^{6}\ \text{J kg}^{-1} = 80\ \text{kW}$$

and this concurs with information given in [4].

The burner being discussed can also use spent cooking oil. This will have a calorific value of about 37 MJ kg^{-1}. Purely for a burner, where heat released is used as such, there is interchangeability of hydrocarbons and vegetable oils and the latter has the advantage of carbon neutrality. For use in an engine, in which heat is converted to work, there are many other factors to be considered. These include the viscosity and its temperature dependence and the cloud point. Neither factor would be at all satisfactory if an attempt was made to use heavy petroleum residue to power a compression ignition engine. Plant oils can, with due attention to quality and possible modification by esterification, be used as a fuel for compression ignition engines. A reader will be aware that this is being widely done around the world.

The entry in the following row is concerned with waste from oil tankers. This chapter is being written during the emergency in the Gulf of Mexico, where oil is leaking copiously from an exploration well. Highly serious though such incidents are, most of the oil contamination of the sea is due not to such mishaps but to operations including cleaning of oil tankers to remove the heavy material which has accumulated at the base. Given that a supertanker holds of the order of 2 million barrels of crude, such wastes summed across the supertankers of the world will be very significant indeed in quantity. The sort of combustion plant described in [5] enables such hydrocarbon waste to be incinerated. The waste will be transferred from the primary tank in which it has accumulated to a smaller one for transfer to the burner. Reference [6] describes a range of burners for such use with performances up to 1500 kW. The last row in the table is concerned with ocean incineration, which of course involves an incinerator mounted on a vessel. The vessel is taken out to sea before the incinerator is operated. Ocean incineration was proscribed by the Inter-Governmental Maritime Organisation (IMO) in 1991 [8].

8.3 Pyrolysis and cracking

A precise distinction between pyrolysis and cracking would be arbitrary, but it is widely known that the latter involves higher temperatures and, very often, a catalyst. In relation to liquid waste treatment the terms do seem, in the research literature and in reports and the like, to be used synonymously and accordingly will be discussed together in this text.

A study in the fairly recent literature [9] is concerned with catalytic pyrolysis of used lubricating oil which, as received, contained significant amounts of soot and also gum and was therefore first treated by filtering and centrifugation. One effect of the pre-treatment was to reduce the sulphur content from 7500 p.p.m. to 1641 p.p.m. If it is desired to have a fuel for compression ignition engines amongst the products the sulphur content is very important. Reference [9] originates in Japan where, at the time the work was published, the maximum allowable sulphur content of diesel was 500 p.p.m. (this has since been reduced). The work used three pyrolysis temperatures: 200, 300 and 400^{o}C. At any one of the three temperatures, pyrolysis of the pre-treated material for one hour over an iron/silica catalyst reduced the sulphur content at least by a factor of two. GC-MS analysis of products from pyrolysis in the presence of a catalyst showed the products to be in the very wide range of about C_5 to C_{25}. Oils pre-treated to remove sulphur as described above gave a higher proportion of lower molecular weight products – up to about C_{10} – than oils having had no such pre-treatment. From the point of view of utilisation of the products carbon number control by catalysis clearly has the potential to improve the viability on a larger scale.

It was described in section 6.3 how biomass and coal can be co-gasified, and similarly waste oil and coal can be co-pyrolysed although such does processing does not of course have any carbon neutrality benefits. Again, an example from the research literature will be considered [10] and the most important points brought out. Of the three classes of pyrolysis product of coal – solid, liquid and gas – one would expect that co-pyrolysing with oil would affect most strongly the liquid part. In [10] this was certainly so; pyrolysis of a particular coal at 650°C gave 15.6% by weight of liquid product, and that rose to 24.3% when at the same temperature the coal was co-pyrolysed with waste lubricant oil. Not only amounts but compositions of the liquid products differed according to whether waste lubricating oil was initially present. For example, whereas the liquid products from coal alone contained phenols in major yield, those from co-pyrolysis with oil contained phenols in much smaller yield indicating that the hydrocarbons in the oil were acting as a hydrogenating agent.

The last research report [11] to be discussed in this section is focused on obtaining fuels in the gasoline boiling range from waste lubricating oil. At temperatures in the range 475-625K in the presence of an alumina catalyst a product termed by the authors of [11] ‘waste oil gasoline’ was obtained which corresponded closely to the properties of a locally obtained commercial gasoline with which it was compared. The comparison is summarised in the table below.

Property	**‘Waste oil gasoline’**	**Commercial gasoline**
Boiling range/K	304-445	312-454
Sulphur content/weight%	0.003	0.002
Calorific value/MJ kg^{-1}	45.9	47.8
Kinematic viscosity/cSt	1.13	1.17
Octane number	96	89
Flash point	245	249
Density/kg m^{-3}	732	735

8.4 Gasification

There has for very many years been manufacture of a general-purpose fuel gas from low-value hydrocarbons such as heavy residue and cracking by-products. This is discussed by the present author elsewhere [12]. This section then will be concerned not with hydrocarbons from processing but with hydrocarbons already having been used, for example as lubricants, and requiring disposal.

As has already been noted, To a good approximation[25] any liquid hydrocarbon material can be taken to approximate in empirical formula to CH_2. Gasification with steam therefore proceeds according to:

$$CH_2 + H_2O \rightarrow CO + 2H_2$$

the product gas being of calorific value about 12 MJ m^{-3} and this continues in places where cheap hydrocarbon feedstock is available.

Interest at the present time in gasification of waste oil is quite limited, probably because unlike the gasification of biomass it does not provide for a bonus in carbon accounting. As an example of a project into gasification of waste oil, it is reported in [13] how waste oil was gasified with water and oxygen at about 800°C. Control of the H_2/CO ratio was necessary as the end use of the gas as to be chemical synthesis not burning. A gas of molar ratio H_2:CO of 1.87 was produced. When a synthesis gas rather than a fuel gas[26] is required it is probable that the synthesis product will be methanol, made according to:

$$CO + 2H_2 \rightarrow CH_3OH$$

and it is stated in [13] that a satisfactory yield of methanol requires that the H_2:CO molar ratio be at least 1.7. The value of 1.87 reported is therefore comfortably above this limit.

8.5 Re-refining

In the USA about 400000 gallons of waste motor oil are disposed of daily [14]. For this and other forms of waste hydrocarbon, re-refining is an option. A relevant point is that refining for the first time, that is refining of crude oil, does not reduce greatly the EROEI of petroleum products. A rough rule is invoked in an earlier chapter that the EROEI of a distillate is that for the crude divided by a factor of about 1.3. This augurs well for re-refining.

Examples of re-refining operations are in the table below. Re-refining is prevalent nor is it new, and the contents of the table are a small representative selection only.

Reference	Details
[15]	Re-refining of used lubrication oil at the only such facility in the western USA. Products for eventual sale ‘light neutral base oil’, ‘mid-range neutral base oil’, ‘asphalt flux’ and ‘light end distillates’ (see below).
[16]	New Zealand: re-refining of vehicle lubricant to produce diesel and base stock. Non-volatile residue used in road building.
[17]	Detailed assessment of the potential for oil re-refining in Japan.
[18]	Wagga Wagga, Australia: a plant re-refining waste oil. Products for fuel use.
[19,20]	Wichita KS: re-refining of used motor oil, 12 million gallons (≈ 0.3 million barrels) annually.

The terms in row 1 need some clarification. ‘Base oil’ is material suitable for lubricant use but requiring adjustment to properties including viscosity to bring it within specification for such use. This adjustment is achieved by blending. The terms ‘light’ and ‘mid-range’ refer to the density or, equivalently, the API gravity. The ‘light end distillates’ are in the diesel boiling range. Asphlatenes comprise the heaviest hydrocarbon compounds in crude oil, having molar masses up to about 1500 g. ‘Asphalt flux’ is used to dilute asphaltenes where they exist in petroleum materials, mitigating their restricting influence on flow. In considering the NZ activity (row two) it is as well to remember that that country has very few hydrocarbon resources indeed, so thrift in hydrocarbon usage is necessary. Re-refining of used lubricating oil in NZ has in fact been taking place for over half a century. In the detailed study appertaining to Japan in reference [17] the following conclusions were noted. Fuel production from re-refining is commercially viable in Japan. Specifications of products of re-refining can be controlled and made the same as the corresponding products from crude oil. On the down side, collection of small amounts of oil for re-refining itself has an energy requirement and, it is noted in [17], diesel powered vehicles for such collection would release sufficient NO_x to incur a penalty having regard to the existence of credits for such pollutants. The Wichita Kansas facility (final row) is a sizeable one, yet the amount of oil it processes in a year is utterly negligible in comparison with the amount of crude oil which the US imports from countries including Canada, Mexico and Venezuela in a single day! There are benefits from oil re-refining as described in this section, but for the practice to reduce dependence on imports[27] would require proliferation of such facilities to an extent that is quite unrealistic.

8.6 Concluding remarks

The world in which we live is dominated by the issue of hydrocarbon availability and usage and no one factor has as strong an influence on world economics as the price of oil. When oil is burned that is the end of it: it has gone to carbon dioxide (and in so doing contributed to CO_2 levels in the atmosphere, a critically important issue in the 21st century) and water vapour. Hydrocarbon having seen non-destructive use has the same calorific value as products from newly refined crude oil and the potential for fuel use is obvious. The processes outlined in this chapter have their parts to play in times of unprecedented preoccupation with hydrocarbon supply and demand.

8.7 References

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9. Incineration of Radioactive Waste

9.1 Introduction

The title of this chapter must not be misunderstood: it does not mean incineration of radioactive substances. Radioactive waste for processing by incineration consists of combustible materials such as fabrics and polymers which have become contaminated with a radioactive substance. When such waste is incinerated the radioactive contaminant remains in the ash, thus its volume is greatly decreased and its manageability improved. In fact volume reduction by a factor of about 100 is expected when radioactive waste is incinerated [1]. The temperature dependence of radioactive processes is extremely weak so they are not accelerated in incineration which is a chemical process providing safe destruction of a substance previously containing radioactive substances.

9.2 Units and amounts

The becquerel (Bq) will be used as the unit of radioactivity throughout this discussion: for those more at home with the curie the conversion is given as a footnote[28].

Now:

$$1\ \text{Bq} = 1\ \text{disintegration per second}$$

or equivalently

$$1\text{Bq} = 1\ \text{s}^{-1}$$

Now Bq is an infinitesimal degree of radioactivity, orders of magnitude lower than that in the air we breathe which is largely due to Radon. The following figures for levels of radioactivity in various substances and media are taken from [2].

	Radioactivity/Bq
The air in a family residence	3×10^3 to 3×10^4
Smoke detector using americium	3×10^4
1 kg of granite[29]	1×10^3
Radionuclide for diagnostic use	7×10^7
Radionuclide for therapeutic use	1×10^{14}
Human body of weight 10 stone	6×10^3

The information in the third row of the table could have been re-expressed 10^3Bq kg^{-1} or, more conventionally, 1 Bq g^{-1}. The radioactivity so expressed is the specific activity and it can be on a volume basis. Clearly when there is incineration the actual activity does not change but the specific activity does, a point which will feature later in this chapter.

9.3 Classifications of radioactive waste

Obviously such classifications differ from place to place and are subject to review. Sources including [3] state that the threshold below which a substance can, for waste disposal purposes, be seen as having nil radioactivity is a specific activity of 100 Bq g^{-1} and a total activity of 4000 Bq. By way of perspective, in the days when watches worked mechanically and lacked any electrical power they sometimes had on the dial paint containing radium and such a watch would release [4] at a few thousand becquerels[30]. A watch weighing 25 g the radium within which had radioactivity 5000 Bq would therefore have a specific activity:

$$5000/25 = 200 \text{ Bq g}^{-1}$$

The half-life of whatever radioactive process is taking place and whether the emitted particles are α or β are relevant to waste classification, and distinction on this basis is made in an International Atomic Energy Agency document [5] which gives 400 to 4000 Bq g^{-1} for the upper limit on the definition of low-level waste (LLW) for isotopes emitting α particles and having long half lives. For radioactive isotopes of long half life with β and γ emission the value defining LLW can be 10^4 Bq g^{-1} or higher. With LLW and intermediate level waste (ILW, more fully discussed below) the concentration of radionuclides is such that their heat release into the waste of which they are a part is negligible.

One sometimes (e.g. [6]) encounters the term very low level waste (VLLW) and this is on the basis that the level is below that formally defining a radioactive substance in certain UK legislation. Reference [6] gives 0.4 Bq g^{-1} for this. The same source defines LLW as having 4000 Bq g^{-1} for an α-emitting waste and as 12000 Bq g^{-1} for a waste emitting β and γ. The distinction between LLW and ILW is a little blurred, but for an α-emitting waste ≈ 10000 Bq g^{-1} would be a reasonable threshold value.

HLW is defined as radioactive waste which releases energy at 2kW m^{-3} or more [7]. This figure is set in context in the calculation in the shaded area below which uses Cs^{137} as an example.

Cs^{137} undergoes decay with β and γ emission and energy 1.174MeV

The density is ≈ 2000 kg m^{-3}

The specific activity of Cs^{137} is 3.4 TBq g^{-1}

1 m^3 of the isotope in pure form has weight 2×10^6 g and activity:

$$3.4 \times 10^{12} \times 2 \times 10^6 \text{ Bq} \approx 7 \times 10^{18} \text{ Bq } (= s^{-1})$$

$$\text{Energy release from 1 m}^3 = 1.174 \times 10^6 \text{ eV} \times 1.6 \times 10^{-19} \text{ J eV}^{-1} \times 7 \times 10^{18} \text{ s}^{-1}$$

$$= 1300 \text{ kW}$$

Hence even Cs^{137} ‘diluted’ by a factor of:

$$1300/2 = 650$$

by whatever medium it is present in would still be classifiable as HLV, not so if it was more heavily ‘diluted’.

9.4 The performance of a typical radioactive waste incinerator plant

It should first be noted that when radioactive waste is incinerated the fuel is whatever substance is holding the radioactive substance in low concentration. Emission of gases such as SO_x, NO_x have to be controlled according to local standards. Also an incinerator might be for radioactive waste only or for simultaneous treatment of radioactive and non-radioactive waste in which case the term ‘mixed’ is used. The German company Nukem manufactures incinerators for radioactive waste disposal [1], [8] and have such installations in countries including (in addition to Germany) Japan, Taiwan and Slovakia. A typical Nukem incinerator burns wood, paper, fabrics, rubber and other ‘conventional’ wastes at 50 kg per hour with bulk densities of 140 to 250 kg m^{-3}. The payload of the incinerator can have concentrations up to 10^{10} Bq m^{-3} of α-emitting radionuclides and up to 10^{12} Bq m^{-3} of β- and γ-emitting radionuclides. Using the mean of the bulk density range given, that is 195 kg m^{-3}, these figures convert to 50 kBq g^{-1} for α-emitting radionuclides and 5 MBq g^{-1} for the β- and γ-emitting radionuclides. When these are compared with values defining LLW and ILW in this chapter it is clear that the capabilities of the incinerator under discussion go beyond either. This means that the incinerator could take wastes having these levels of radioactivity, or wastes themselves having higher levels blended with uncontaminated waste to bring the radioactivity levels of the bulk to within the incinerator specifications.

The ash yield from the incinerator under discussion [1] will be about 8%, and this will have a specific activity on a weight basis:

$$100/8 = 12.5$$

times higher than that of the initial contents of the incinerator. It will however have a much smaller volume and the ash residue can be distributed at a landfill at whatever proportion is necessary to bring the specific activity into the VLLW range or even lower than that. That is what is meant by the improved ‘manageability’ of radioactive waste by incineration referred to at the beginning of this chapter.

The *raison d'etre* of a radioactive waste incinerator is entrapment of the radioactive isotopes in the ash and loss of any ash as particles of micron size ('fly ash') in the post-combustion gases would clearly represent a degree of loss of function of the incinerator. This point is examined in the calculation below.

We approximate the composition of the non-radioactive waste which is the fuel to that of cellulose, formula $C_6H_{10}O_5$. This has formula weight 162 g, and a routine calculation of the amount and composition of flue gas following combustion of 1 kg of it follows.

Element	Amount in moles in 1 kg of the cellulosic waste	Oxygen requirement for combustion/mol
C	(72/162) × 1000/12 = 37	37, for: $C + O_2 \rightarrow CO_2$
H	(10/162) × 1000/2 = 31 (expressed as H_2)	15.5, for: $H_2 + 0.5O_2 \rightarrow CO_2$
O	(80/162) × 1000/32 = (expressed as O_2)	‘-15’

Continuing into the boxed area below:

Total oxygen requirement for stoichiometric combustion = 37.5 mol. Total oxygen for combustion with (as would be usual) 20% excess air = 45 mol

Accompanying nitrogen in a quantity = (45 × 3.76) = 169 mol

Total dry gas from combustion of kg of the waste:

CO_2 37 mol, O_2 7.5 mol, N_2 169 mol. Total 213.5 mol or 5 m^3 at 288K 1 bar

Now it was noted earlier that the incinerator under review operates in the range of specific activities 50 kBq g^{-1} to 5 MBq g^{-1}. The geometric mean of these is:

$$[(50 \times 10^3) \times (5 \times 10^6)]^{0.5}\ \text{Bq g}^{-1} = 500000\ \text{Bq g}^{-1} \text{ or } 500\ \text{kBq g}^{-1}$$

and this value will be used in the calculation which follows. 1 kg of the waste when processed would leave 80 g of ash having specific activity 6.25 MBq g^{-1} or actual activity 500 MBq. In the purely hypothetical case[31] where 1% of the ash finished up in the flue gas, the gas would have a specific activity:

$$[(500/100)/5] \times 10^3\ \text{kBq m}^{-3} = 1000\ \text{kBq m}^{-3}$$

The value in the calculation of 1000 kBq m^{-3} greatly exceeds the background level in the atmosphere which, largely by reason of the radon, is about 1 kBq m^{-3} (≈ 1 Bq g^{-1}). Flue gas from the incinerator will of course be diluted on discharge to the atmosphere but even so control of particle emission is required. This often uses a fabric filter [11].

9.5 Concluding remarks

The way in which incineration can render radioactive waste safe has been outlined in this chapter. Where a suitable incinerator is in operation waste can be imported for disposal, and obviously the 'import' becomes in effect an export in that revenue is raised. There are proposals for this in the US and a reader going to [9] and to [10] will be introduced to the pros and the cons.

9.6 References

[1] 'Incineration of radioactive waste' NUKEM Technologies GmbH 2007 (available online in pdf form)

[2] http://www.world-nuclear.org/education/ral.htm

[3] http://www.enviroserv.co.za/pages/content.asp?SectionID=508

[4] http://www.hps.org/publicinformation/ate/q1697.html

[5] http://www-pub.iaea.org/MTCD/publications/PDF/Pub1419_web.pdf

[6] Kemp R., O'Riordan T. 'Planning for radioactive waste disposal' Land Use Policy 5 37-44 (1988)

[7] **'**Fundamentals of the management of radioactive waste: An introduction to the management of higher-level radioactive waste on nuclear licensed sites' HSE, UK (2007)

[8] 'Treatment centres for radioactive waste' NUKEM Technologies GmbH 2007 (available online in pdf form)

[9] http://leanweb.org/news/latest/company-to-import-and-export-nuclear-waste-through-port-of-new-orleans-2.html

[10] http://www.nuclearwastenews.com/view_article.asp?artID=5730

[11] 'Design and Operation of Radioactive Waste Incineration Facilities' Safety Series No. 108, International Atomic Energy Agency, Vienna (1992)

Postscript

Waste treatment is an area in which two very important factors unite. One is health, for the obvious reason that wastes not suitably disposed of threaten health. The other is energy, as many wastes have potential fuel use with the advantage of carbon neutrality at a period when ‘critical’ would not be too strong a word to apply to the world energy situation. On the day in late 2007 when the price of oil crossed $100 per barrel for the first time that was seen by some as portending loss of control in world affairs. At the time of writing this preface in May 2010 the OPEC basket price is $77.53 per barrel and the dismal prophecies of two and a half years ago have not come to pass.

Nevertheless, that there is in the collective consciousness of the world extreme sensitivity to the matter of oil availability is clear. So in times very distant from our own it was with rubbish. For example, middens from the late bronze age and the early iron age contain artefacts some of which, it is believed, were placed there as votive offerings[32]. A midden would also be the site of community feasts and that gives it a spiritual significance.

Whilst the author hopes that readers will want to share such thoughts as those in the previous paragraph (and perhaps even develop them further for themselves) they have to be followed by a return to the applied science which is the content of the book. Landfill sites are becoming less plentiful and in any case landfill disposal has greenhouse gas disadvantages as explained in the main text. That thermal processing disposes of waste effectively and provides energy as a major bonus has been the thrust of this book.

Endnotes

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[1] Probably reflecting the restaurant culture of this Asian capital.

[2] Tyre-derived fuel (TDF) features in Chapter 4.

[3] That it the largest in the US is certain.

[4] Where any facility provides both electricity and heat there is an important distinction to be understood. Such a facility does not necessarily use Combined Heat and Power (CHP) in the thermodynamic sense of that term. In CHP some of the energy lost through the restricted efficiency of conversion of heat to work is recovered in what is termed a CHP cycle. This contrasts with the practice of raising steam and diverting some of it to power generation using a Rankine cycle and some to heating in two independent operations.

[5] On the web page:

http://www.usp.nus.edu.sg/global_programme/past_events/ay03-04/Tuas.html

originating at the National University of Singapore it is asserted that Tuas South is the largest waste incineration facility in the world.

[6] An alternative term to pelletised RDF is d-RDF, where d stands for ‘densified’. See:

http://wmr.sagepub.com/cgi/reprint/14/3/311.pdf

[7] The author is of course aware that a correction can be made for the vapour in equilibrium with liquid water at 25°C, but such a correction will not materially improve the calculation being performed.

[8] p.p.h.m. = parts per hundred million.

[9] Tyre-derived fuel (TDF) has a section to itself in the next chapter.

[10] Sometimes methane from landfills is collected for use as a gaseous fuel, in which case the term ‘landfill gas’ applies. Landfill gas originating from cellulosic waste is a carbon-neutral form of methane. Methane originating as natural gas is not of course carbon-neutral.

[11] It is widely believed that Brazil will sooner or later become an OPEC country.

[12] About a fifteen per cent of that is hydroelectric [21].

[13] Not the best term: ‘calorific value’ is meant.

[14] Though certainly a peer-reviewed set.

[15] 1 barrel (bbl) = 0.159 m^3

[16] Whilst it can be unsound to argue from regional to worldwide trends, the author will point out that when the only refinery in Scotland was closed down by a strike in 2008 effects on day-to-day life in Scotland were not major [27].

[17] There was much R&D in the nineteen-eighties into solar drying of such slurry to make a hard product as an alternative to coal briquettes. This required production in the warmer months and stockpiling for the colder months when 'solar drying' might not be possible. Commercialisation was limited.

[18] The distinction between tars and oils is fairly arbitrary being based on degree of solubility in certain hydrocarbon solvents.

[19] Not for nothing did Albert Einstein say in 1949 (present author's italics):

> 'A theory is the more impressive *the greater the simplicity of its premises*, the more varied the kinds of things that it relates and *the more extended the area of its applicability*. Therefore classical thermodynamics has made a deep impression on me . . . .'

See: http://www.upscale.utoronto.ca/GeneralInterest/Harriso/LifeEnergy/LifeAndThermo.html

[20] The term 'carbon-neutral by paternity' has been coined for such substances, also for synthesis gas made from biomass.

[21] The quantity calculated represents about 5% of the annual electricity consumption of Stavanger [2].

[22] When natural gas production in the Bass Strait began.

[23] It is Japan's smallest city.

[24] This matter of burner efficiency is easily misunderstood and such terms as 'radiation losses' are often used rather imprecisely to explain it. The present author's understanding is this. If fuel was supplied at the rate specified and combustion was complete the heat release rate must by the principles of thermochemistry be the higher of the two values calculated above. Such burners usually operate with significant excess air and this has the effect of lowering the flame temperature. About a third of the heat from the flame will be transferred to the surroundings by radiation and a cooler flame makes for much lower radiation because of the T^4 dependence of the radiation. Also, the radiative flux (units W m^{-2}) will, unlike the total radiation (units W), have a dependence on the flame shape. If therefore flux is the basis of flame performance assessment the flame shape will have an effect. It is clear from [3] that in the experimental trials described therein combustion was complete so the factors in this f.n. are relevant even if they do not enable the value of 17.7 kW to be reproduced by calculation.

[25] In gas radiation this approximation is made, and leads to the result that when a hydrocarbon liquid is burnt the post-combustion gas is equimolar in CO_2 and H_2O.

[26] In the contemporary literature the term 'syngas' is often used irrespective of the intended purpose.

[27] Such a claim is made in [20].

[28] Using the symbol Ci for curie:

$$1\ \mathrm{Ci} = 2.2 \times 10^{12}\ \mathrm{minute}^{-1} \text{ or } 3.7 \times 10^{10}\ \mathrm{s}^{-1}$$

$$1\mathrm{Bq} = 2.7 \times 10^{-11}\ \mathrm{Ci}$$

[29] Residents of Aberdeen (a.k.a. the granite city) are aware of the unusually high radioactivity level of granite and that it is insufficient to endanger health.

[30] Persons employed at applying the paint did sometimes experience serious health effects and there was litigation.

[31] This hypothesis is entirely the author's own for pedagogic purposes and has no basis at all in the published details of the incinerator being considered.

[32] The author owes this information to Dr. Kate Waddington of Bangor University.