

Packaging — Optimization of energy recovery from packaging waste

ICS 13.030.99; 55.040

National foreword

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This Published Document was published under the authority of the Standards Policy and Strategy Committee on 4 June 2004

Summary of pages

This document comprises a front cover, an inside front cover, the CR title page, pages 2 to 26, an inside back cover and a back cover.

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

© BSI 4 June 2004

ISBN 0 580 43781 7

ICS

English version

Packaging - Optimization of energy recovery from packaging waste

Emballage - Optimisation de la valorisation énergétique des déchets d'emballages

Verpackung - Optimierung der energetischen Verwertung von Verpackungsabfällen

This CEN Report was approved by CEN on 2 June 1999. It has been drawn up by the Technical Committee CEN/TC 261.

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Foreword

This document has been prepared by CEN /TC 261, "Emballage".

This document is actually submitted to the publication.

Introduction

The Directive on Packaging and Packaging Waste, Annex II, 3(b) states that *Packaging waste processed for the purpose of energy recovery shall have a minimum inferior calorific value to allow optimization of energy recovery* (Ref. 1).

The Commission's Mandate M 200 Rev. 3 asks CEN to propose a standard on *Requirements for packaging recoverable in the form of energy recovery, including specification of minimum inferior calorific value* (EN 13 431).

Energy recovery is defined in Article 3.8 of the Directive : *'energy recovery' shall mean the use of combustible packaging waste as a means to generate energy through direct incineration with or without other waste but with recovery of the heat.*

EN 13431 shall apply to packaging placed on the market in order to allow optimization of energy recovery of packaging waste by specifying minimum inferior calorific value and other supplementary requirements. It cannot and does not consider conditions or contaminants of packaging waste at arrival to furnace at the energy recovery plant.

1 Scope

The objective of this report is to identify and define properties of packaging and packaging waste to allow optimization of energy recovery.

This report takes a wide approach to the process of energy recovery in order to identify the items to be standardised according to the Directive and the Mandate.

2 Terminology

Net calorific value (inferior calorific value), Q_{net} : defined in ISO 1928 :1995 (Ref. 3).

Required energy H_a : energy necessary to adiabatically heat the post combustion substances of a material and excess air from ambient temperature to the specified final temperature.

Calorific gain : the positive difference between the energy released on combustion of a material (the net calorific value) and H_a .

Available calorific gain : recovered heat providing useful energy.

3 Packaging and packaging waste

The statement in Annex II of the Directive quoted above refers to **packaging waste**, whereas the Mandate wording refers to **packaging**. Packaging waste can be used for energy recovery, but it is the packaging placed on the market that has to meet the specific requirements for energy recovery and therefore is subject to meeting the standard. The link between the Directive and the Mandate can be described in the following manner :

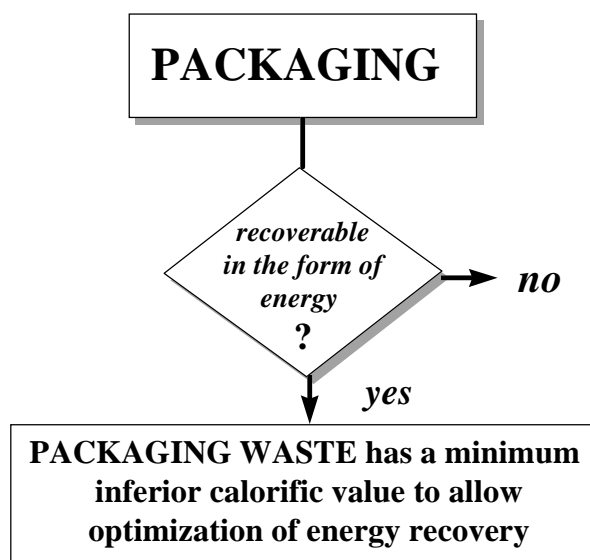


Figure 1

As shown in Figure 2, packaging materials, packaging, used packaging and packaging waste form a sequence from production and consumption to waste, without intrinsic change of the chemical material properties which are essential for energy recovery.

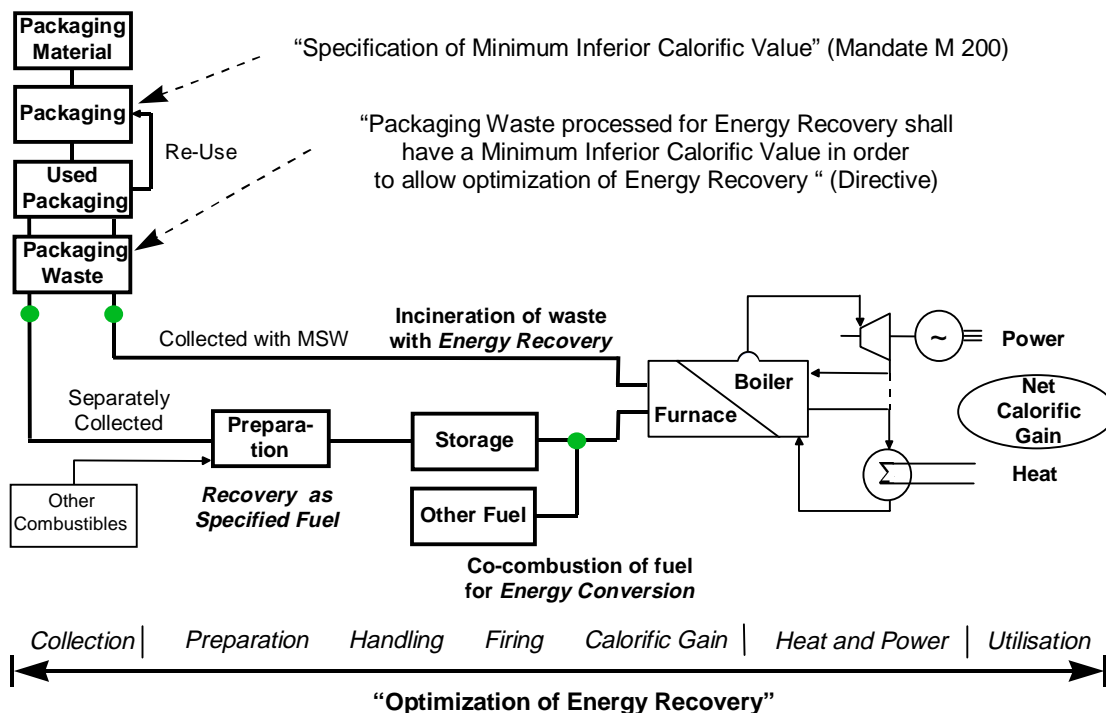


Figure 2 - The Overall System of Optimization of Energy Recovery

4 Optimization of energy recovery

The objective of this report is to identify and define properties of packaging and packaging waste to allow optimization of energy recovery. **Optimization of Energy Recovery** from packaging waste involves the overall system including properties of packaging, waste collection systems, preparation, storage and energy conversion to provide net calorific gain as shown in Figure 2. Some steps included in the overall system are not related to the packaging itself, and therefore not considered influential to the requirements of the packaging. Combustion plants, for example, are subject to specific regulation and the use of produced energy depends on local circumstances.

Figure 3 shows the relationship between packaging, packaging waste and their relevant requirement in the framework of the overall system of optimization of recovery in the form of energy. These issues are discussed in detail in the following.

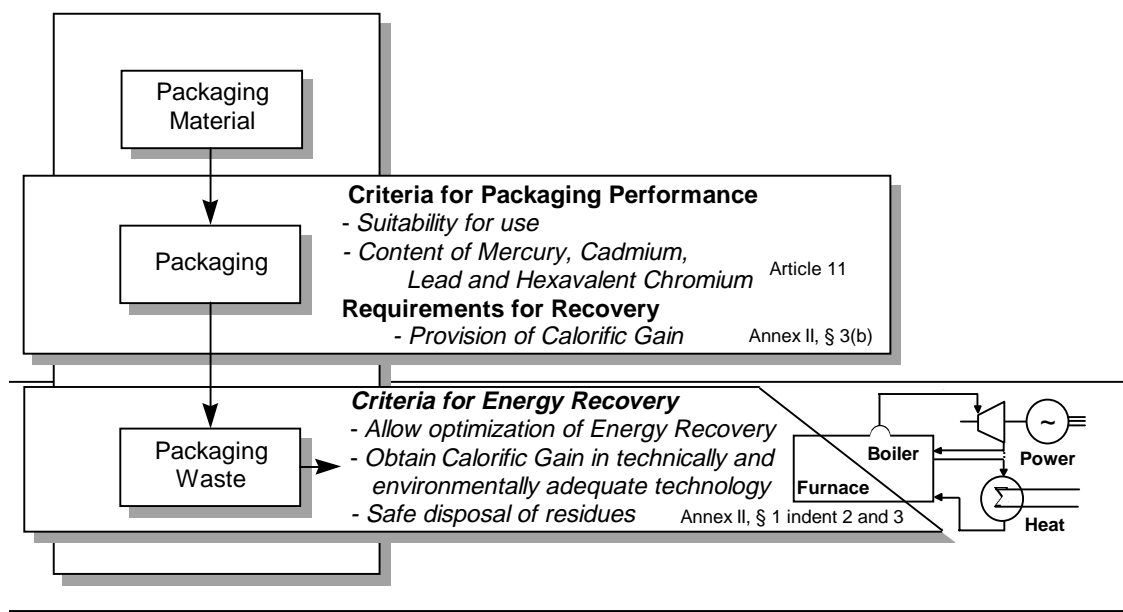


Figure 3 - Relevant Issues of Directive of Packaging and Packaging Waste and Mandate M 200 Rev. 3

Collection system and preparation

In order to optimize energy recovery from used packaging, the waste collection system should be designed and managed so that the energy content and other fuel properties of used combustible packaging are preserved. The extent of preparation necessary to transform packaging waste into a fuel, depends on the requirements of the actual energy conversion plant.

Today, two different methods of collection and preparation or pre-treatment are prevailing (Figure 2) :

- 1) packaging waste is collected with other Municipal Solid Waste (MSW) for direct incineration in MSW incinerators. This type of incinerator is efficient, proven and requires little pre-treatment of the mixed waste ;
- 2) separation of combustible waste gives a combustible fraction, known as Refuse-Derived Fuel, RDF. Source separation and preparation of combustible packaging waste allows for the production of an energy-rich solid fuel with specific properties (Packaging-Derived Fuel, PDF).

These derived fuels can be used as a single fuel or used in co-combustion with other fuels in existing solid fuel fired combustion systems. In all these processes, combustible packaging waste substitutes primary fuels.

Energy conversion and generation of net calorific gain

Energy conversion of chemically bound energy to generate net calorific gain consists of three main process steps :

- combustion of a fuel in a combustion chamber, resulting in hot flue gases and solid residues, such as ashes and slag ;
- utilization of the heat content of the hot gases in a heat recovery system ;
- conversion of the recovered heat to provide end-use energy in the form of electricity and/or heat.

Combustion

Combustion efficiency is related to the degree of completeness of combustion. It is mainly affected by fuel particle size, fuel-to-air ratio, temperature, residence time and turbulence (mixing of fuel and air) in the furnace. Products of incomplete combustion are carbon monoxide, volatile organic compounds and soot particles in flue gas and unburnt carbon in ashes and slag. In the combustion process, organic substances are decomposed and transformed into gaseous components. Depending on the combustion conditions, inorganic compounds are either unaffected or transformed into insoluble oxides, sulphides, or water-soluble chlorides and sulphates. High combustion efficiency therefore means minimisation of these pollutants.

In grate fired mass burn systems the dominant part of ash leaves the furnace in the form of bottom ash (slag). The amount of organic carbon in bottom ash is low, and the slag may be used for construction applications. High temperature and the presence of acid components volatilise certain heavy metals, e.g. cadmium and zinc, from the bottom ash to fly ash and filter residues. This can be seen as a positive clean-up effect of the slag (Ref. 4). Fly ash and filter residues always contain high concentrations of fuel pollutants and require special treatment. In accordance with current regulations, modern Waste-to-Energy plants are well equipped to deal with these pollutants in an environmentally sound way (Ref. 5).

Utilization of the heat content of combustion gases

The heat content of combustion gases is recovered in the boiler as steam or hot water. The heat exchange efficiency is proportional to the temperature difference between the hot and cold sides of the system. General aspects on generating net calorific gain are :

- the facility is designed for a specified type, quality and range of fuel. A fuel that is unsuitable for the actual equipment may affect the energy recovery process negatively and cause fouling, slagging and corrosion in the boiler. As a result, frequent soot blowing and shut downs for mechanical clean-up and repair work will be necessary. This reduces the plant availability ;
- the internal energy consumption of blowers, pumps, extensive flue gas cleaning equipment etc. reduces overall efficiency and the net calorific gain.

Overall efficiency and net calorific gain are optimized by minimising thermal losses, e.g. by :

- extensive cooling of the hot flue gases in the boiler ;
- utilization of the remaining heat in the flue gases after the boiler for drying and preheating of the fuel, or for other process steps.

Conversion of thermal energy to electricity and/or useful heat

The efficiency of energy conversion to electricity and/or heat depends on temperature and pressure of generated steam.

Combined generation of electricity and steam or hot water for heating purposes gives overall energy utilization of more than 70 %. This combination is favourable to the optimization of energy recovery. Condensation of water vapour in the flue gases may further increase energy utilization.

5 Requirements for packaging recoverable in the form of energy

Calorific Gain

The principal requirement for packaging to be recoverable in the form of energy is that it is combustible under ordinary conditions (Ref. 6). and, in order to allow optimization, capable of providing calorific gain. This means that the net heat of combustion, Q_{net} , of the packaging shall exceed the energy required, H_a , to raise the temperature of its combustion products, residues and excess air to the required temperature, as given in Ref. 5. This is evaluated in Chapter 6 and is true for all organic materials and most multi-material light-weight packaging containing a major amount of organic material.

Ash content

The energy recovery process gives a substantial total reduction of the volume of waste and provides slag that may be recycled. Average combustible packaging has an ash content lower than MSW or coal. The requirement for calorific gain, by implication, limits the total ash content. The limit varies according to the packaging composition (see Table 1 and examples in Chapter 9). Efficient combustion limits the content of unburnt organic matter in ash, and as a result only little energy is lost in slag and ash residues. The ash content of packaging is therefore not an important issue with respect to optimization of, or suitability for energy recovery.

Other supplementary requirements

Other supplementary requirements could be on acid forming substances, heavy metals and other hazardous substances in combustible packaging. These subjects are covered in Ref. 6. The following can be stated :

- the content of acid forming substances, i.e. sulphur, nitrogen and chlorine, in the fuel feed to an energy conversion plant is determined by the design and regulated emission limits of the plant. MSW incineration plants are equipped to deal with average packaging waste. The final disposal of residues from incineration is also subject to regulation ;
- the fate of heavy metals in incineration is thoroughly described in Refs. 4, 7 and 8. The emission of these is regulated. Heavy metals do not normally play a major functional role in combustible packaging materials, since a major part of which is used for food application. Mercury, cadmium, lead and hexavalent chromium are regulated in Article 11 of the Directive (Ref. 1) ;
- any other hazardous components, that may be present in packaging waste, will be decomposed by the high temperature of the combustion process.

6 Theoretical determination of calorific gain

According to the definition in Ref. 6, a combustible material is defined as capable of releasing energy by burning. By standard thermodynamic procedure, its characteristics as an energy generator can be calculated. In order to allow optimization of energy recovery the released energy must be high enough to provide calorific gain in the combustion process.

The net heat of combustion (net calorific value), Q_{net} , of a material is the amount of heat released when it burns and when all water remains in the gas phase. It depends on chemical composition of the material. The rate of heat release also depends on the physical properties of the material. In order to provide calorific gain, Q_{net} , of a material shall exceed the amount of energy required, H_a , to adiabatically raise the temperature of the post-combustion substances (including excess air) from ambient temperature to the specified final temperature. A calorific gain is obtained when Equation (1) is fulfilled :

$$Q_{net} - H_a > 0 \quad (1)$$

The **net calorific value** of a packaging consisting of different constituents can be calculated according to Equation (2) :

$$Q_{net} = \sum_{i=1}^n f_i Q_{net,i} \quad (2)$$

where

Q_{net} net calorific value of the packaging ;

f_i fraction of constituent i in the packaging ;

$Q_{net,i}$ net calorific value of constituent i of the packaging.

Combustible packaging may contain non-combustible materials, of inert or reactive nature, that may have a negative effect on the calorific gain. H_a for a packaging material may be calculated according to Equation (3) :

$$H_a = \sum_{j=1}^m g_j C_{p,j} \cdot (T_a - T_o) \quad (3)$$

where

H_a energy required to adiabatically heat combustion products, residues and excess air from T_o to T_a ;

- g_j ratio of combustion products and residues (flue gases and ashes) and excess air ;
- $C_{p,j}$ specific heat capacity of post combustion product j at constant pressure ;
- T_a the final combustion temperature ;
- T_o the ambient temperature.

Equation (3) is valid for an adiabatic situation. For the purpose of the EN Standard on Requirements for packaging recoverable in the form of energy (Ref. 9) this equation is used to estimate calorific gain of packaging.

H_a of a packaging consisting of different constituents can be calculated according to Equation (4) :

$$H_a = \sum_{i=1}^n f_i H_{a,i} \quad (4)$$

where

- H_a energy required to adiabatically heat the combustion products, residues and excess air from T_o to T_a ;
- f_i fraction of constituent i in the packaging ;
- $H_{a,i}$ energy required to adiabatically heat the combustion products, residues and excess air from T_o to T_a of constituent i of the packaging.

For a more elaborated explanation on calorific gain and methods of calculation, see standard textbooks on thermodynamics and Annex A.

7 Identification of the minimum inferior calorific value

The *minimum inferior calorific value*, $Q_{net,min}$, is **identified** as H_a , i.e. :

$$Q_{net,min} = H_a \quad (5)$$

The minimum inferior calorific value is material specific and depends on combustion conditions. Thus there is no universal minimum inferior calorific value. For the EN Standard on Requirements for Packaging Recoverable in the Form of Energy Recovery (Ref. 9), the conditions required in Ref. 5 are used.

8 Theoretical and practical implementation

When Equation (1) is fulfilled, the Q_{net} of a combustible material is sufficient to provide calorific gain in a given combustion system.

Ref. 10 reports the energy required to achieve different combustion temperatures for MSW of different composition. The curve in Figure 4 shows typical H_a values for different temperatures. Q_{net} of MSW, being usually in the range 8-12 MJ/kg, is sufficient for reaching combustion temperatures of 1200 °C, which is well above the minimum combustion temperature of 850 °C as specified in Ref. 5.

In order to maintain optimum operation of existing Waste-to-Energy plants it is important to keep the net calorific value of the mixed feed within the design range of the incinerator, i.e. 8 - 12 MJ/kg. This can be achieved by leaving the high calorific, combustible packaging waste from households in MSW.

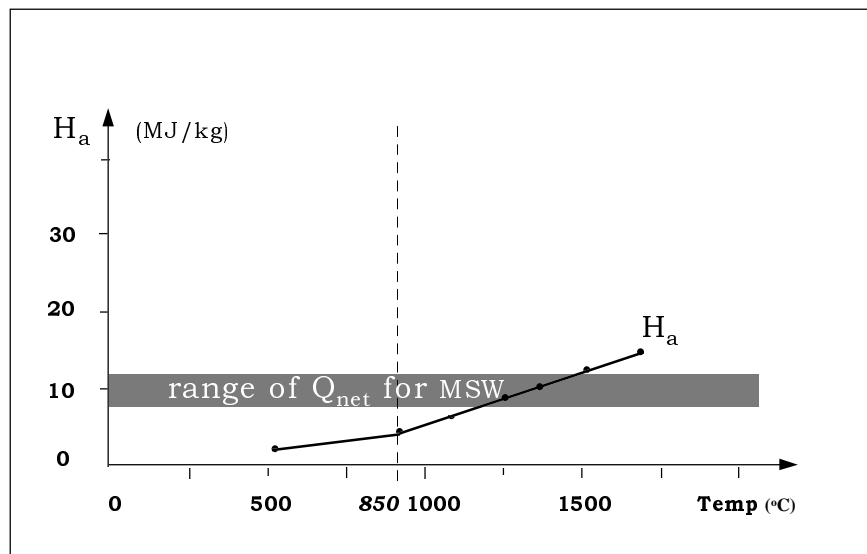


Figure 4 - The curve shows typical H_a values for MSW of different compositions incinerated in an MSW incinerator at different temperatures. Data obtained from practical experiences (Ref. 10)

In Figure 5 a, the relevant energy values for different combustible packaging materials and fuels are compared. For all materials and fuels shown, the values of Q_{net} exceeds that of H_a , and Equation (1) is fulfilled. Furthermore, H_a exceeds the total losses in typical waste incinerators. The available calorific gain as obtained in practice is in reality higher than the theoretically calculated calorific gain (Figure 5.b). This demonstrates that the requirement for packaging recoverable in the form of energy as defined in Chapter 5, i. e. providing calorific gain, is a conservative approach.

Comparison of net calorific values (Q_{net}) and energy content of materials

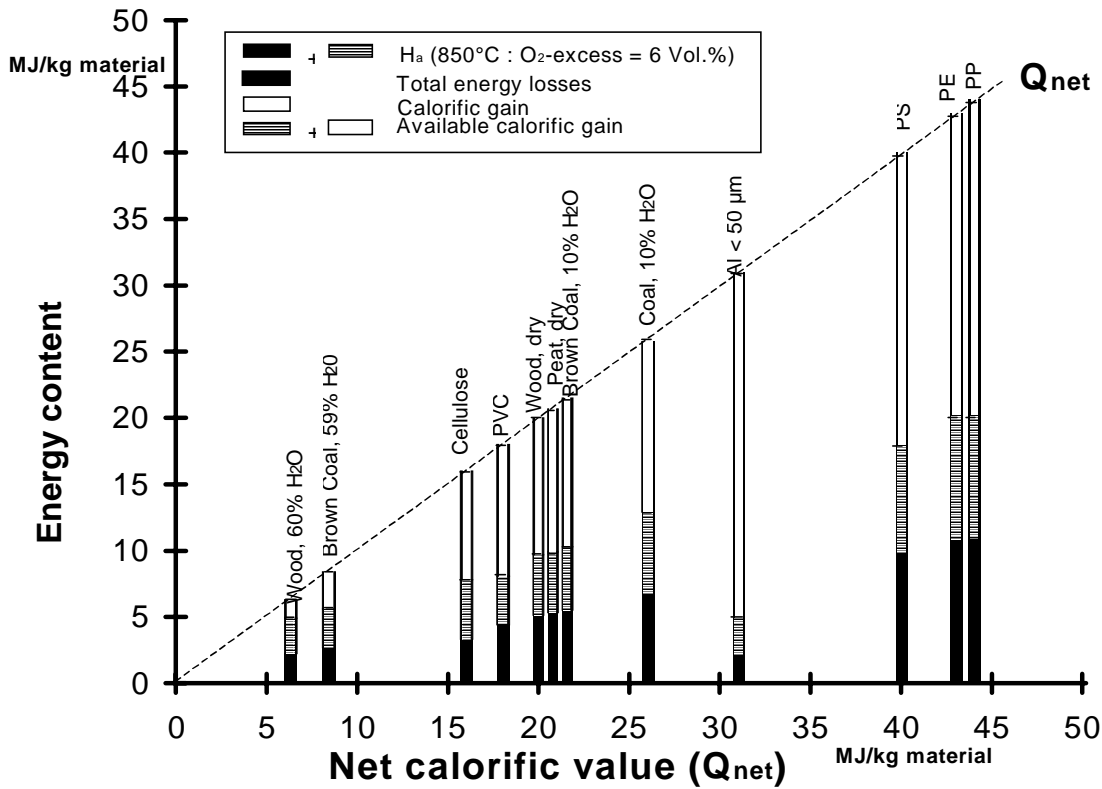


Figure 5 a- Comparison of net calorific values (Q_{net}) with the energy content (H_a) of their flue gases at 850°C and 6 % excess oxygen for some packaging materials and fuels and with the heat losses

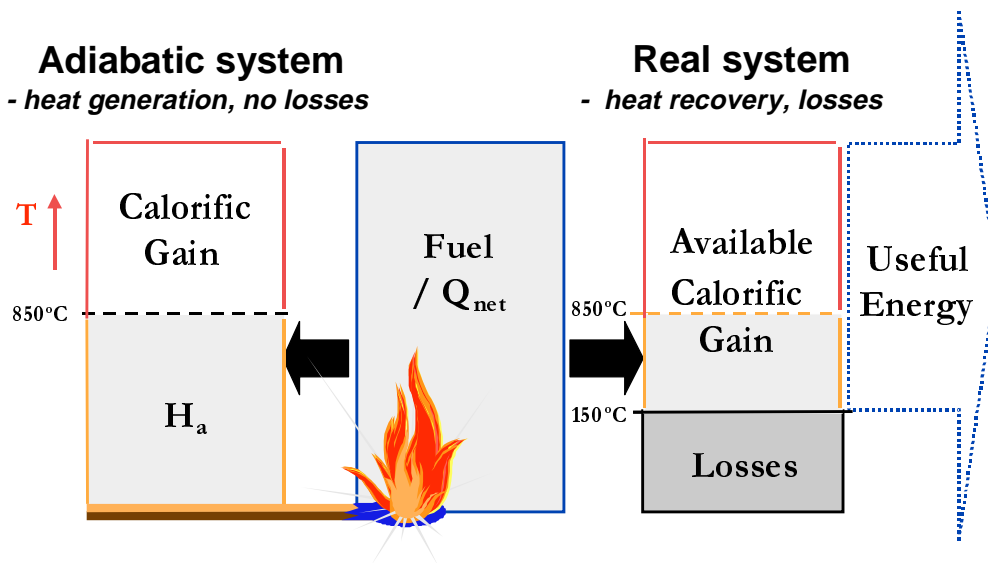


Figure 5 b - Calorific gain and available calorific gain at a specified temperature and oxygen content of the flue gas

9 Determination of calorific gain

Q_{net} is material specific and may be determined by standard methods, e.g. by calorimetry (Ref. 3). Data for most materials are available in the literature (e.g. Ref. 11).

H_a for an assumed final temperature and amount of excess air, is material specific and may be obtained by Equation (3). The Council Directive on Incineration of waste Plants (Ref. 5) provides that combustion temperature must be at least 850 °C and excess oxygen higher than 6 %. These minimum conditions are used for the calculation of calorific gain of packaging materials.

Table 1 shows Q_{net} and H_a at 850 °C and 6 % excess oxygen in the flue gas for some packaging materials, inert materials and moisture.

Table 1 - Typical Q_{net} , H_a and differences calculated for an ambient temperature of 25 °C and a final specified temperature of 850 °C at 6 % O₂, of some packaging materials and constituents. In case of a positive difference there is a calorific gain.

Constituent	Q_{net} (MJ/kg)	H_a (MJ/kg)	$Q_{net} - H_a$ (MJ/kg)
Paper constituents :			
- cellulose	16	8	8
- lignin	26	12	14
Plastics :			
- polyethylene, PE	43	21	22
- polypropylene, PP	44	20	24
- polystyrene, PS	40	18	22
- polyvinyl chloride, PVC	17	8	9
- polyethylene terephthalate, PET	22	10	12
Aluminium (combustible) ^a	31	6	25
Aluminium (inert) ^b	0	1	-1
Steel (inert)	0	0,4	-0,4
Other inert material (ceramic, glass etc)	0	1	-1
Calcium Carbonate ^c	-2	1	- 3
Water (as moisture)	-2	2	- 4
^a Thin gauge aluminium up to 50 µm is calculated as combustible. ^b Aluminium over 50 µm is calculated as not combustible. ^c During the combustion process, calcium carbonate forms calcium oxide and carbon dioxide endothermatically.			

For packaging made of multi-materials, Eq :s 1-4 can be used to determine whether it provides calorific gain or not. Some examples of calculation of typical calorific gain for multi-material packaging :

EXAMPLE 1	Composition :	Cardboard (66 % cellulose, 23% lignin) with 11% inert coating
	Calorific gain :	$0,66 \times 8 + 0,23 \times 14 + 0,11 \times (-1) = 8 \text{ MJ/kg}$
	Ash content :	11 % (inert coating)
EXAMPLE 2	Composition:PP with 50 % carbonate filler	
	Calorific gain :	$0,5 \times 24 + 0,5 \times (-3) = 10,5 \text{ MJ/kg}$
	Ash content :	30 % (CaO from CaCO_3)
EXAMPLE 3	Composition :	PS with 2 % TiO_2
	Calorific gain :	$0,98 \times 22 + 0,02 \times (-1) = 22 \text{ MJ/kg}$
	Ash content :	2 % (TiO_2)
EXAMPLE 4	Composition :	Laminate of 71 % PE, 12 % Al and 17 % PET
	Calorific gain :	$0,71 \times 22 + 0,12 \times 25 + 0,17 \times 12 = 21 \text{ MJ/kg}$
	Ash content :	23 % (Aluminium oxide)
EXAMPLE 5	Composition :	Laminate of 49 % PE, 22 % Al and 29 % PET
	Calorific gain :	$0,49 \times 22 + 0,22 \times 25 + 0,29 \times 12 = 20 \text{ MJ/kg}$
	Ash content :	41 % (Aluminium oxide)

10 Conclusions

I Optimization of Energy Recovery from packaging waste in the wide sense means that process equipment and overall management are optimized to utilise the energy content of combustible packaging waste to provide net calorific gain. This includes properties of packaging, collection system, preparation, storage and energy conversion to useful energy for a specific need.

Some steps included in the overall system, but not directly related to the packaging itself, i.e. collection and preparation systems, utilization of the heat content, conversion of the energy into useful heat and/or power are not considered influential on the requirements for packaging.

In order to maintain optimum operation of existing Waste-to-Energy plants it is important to keep the net calorific value of the mixed feed within the design range of the incinerator, i.e. 8 - 12 MJ/kg. This may be achieved by leaving the high calorific, combustible household packaging waste in MSW.

II The minimum inferior calorific value of a packaging is identified to be the amount of energy, H_a , sufficient to adiabatically heat up its gaseous combustion products, residues and excess air from ambient temperature to the final temperature. This value can be calculated for given conditions, e.g. as specified in Ref. 5. It is material specific and depends on the chemical composition of the packaging. There is no universal value.

III Packaging made of organic material has a net calorific value, Q_{net} , that exceeds the minimum inferior calorific value and is capable of providing calorific gain. It is therefore **recoverable in the form of energy and suitable for optimization of energy recovery**. The suitability for energy recovery of packaging made of multi-materials, including both organic and inorganic materials, can be verified by calculation.

IV The net calorific value of a packaging can be measured by standard methods (Ref. 3 or equivalent) or calculated by Equation (2).

V The energy recovery process gives a substantial total reduction of the volume of waste and provides slag for recycling. The requirement for calorific gain, by implication, limits *the ash content* of packaging recoverable in the form of energy. The limit varies according to the packaging composition. The ash content is not an important issue with respect to optimization of, or suitability for energy recovery. Only little energy is lost in slag and ash residues and the requirements for a calorific gain takes due account of it. Average combustible packaging has an ash content lower than MSW or coal.

VI The content of **acid forming substances**, i.e. sulphur, nitrogen and chlorine, in the fuel feed to an energy conversion plant is determined by the design and regulated emission limits of the plant. MSW incineration plants are equipped to deal with average packaging waste. The final disposal of residues from incineration is also subject to regulation. Therefore, a supplementary requirement for acid forming substances for packaging recoverable in the form of energy recovery is unnecessary.

VII Heavy metals do not normally play a major functional role in combustible packaging materials. The Packaging Directive regulates the content of mercury, lead, cadmium and hexavalent chromium in packaging.

VIII Any **other hazardous constituents**, that may be present in packaging waste, will be decomposed by the high temperature of the combustion process.

IX Energy conversion plants have to comply with regulations with respect to the **quality of combustion and to flue gas treatment**. A high calorific value contributes to the quality of combustion. Particles, acid forming constituents and other pollutants, i.e. heavy metals, originating from the fuel, have to be effectively removed from the exhaust gases and be safely disposed of. This treatment requires energy and reduces the available calorific gain.

Annex A (normative)

The Calorific Gain and Method of Calculation

Abstract

In this report, a detailed account is given of how the amount of heat, later defined as minimum inferior calorific value ($H_a = Q_{net,min}$) required for adiabatically heating all post-combustion products of a packaging (P) from ambient temperature (T_o) to a defined final temperature (T_a) is calculated. Counting pure constituents i , including water (moisture) and fillers, $H_a(P)$ is given by the equation :

$$H_a(P) = \sum_{i=1}^n f_i H_{a,i}$$

where f_i is the fraction (most naturally the mass fraction, w_i) of the i -th constituent of P . In the same way the net heat of combustion, Q_{net} , of a compound packaging can be obtained from the equation :

$$Q_{net}(P) = \sum_{i=1}^n f_i Q_i$$

where Q_i denotes chemical (e.g., net heat of reaction, $Q_{net,i}$, or heat of dissociation, $Q_{d,i}$) or physical (e.g., heat of vaporization, $Q_{vap,i}$) heat of reaction associated with the i -th constituent.

The determining quantity of the proposed CEN energy recovery criterion is the *calorific gain*, ΔQ , which is defined as :

$$\Delta Q \equiv Q_{net} - H_a(P) = \sum_{i=1}^n f_i (Q_i - H_{a,i}) > 0$$

The Q_{net} values are basically determined calorimetrically, the H_a values are calculated with the aid of isobaric specific or molar heat capacity data, C_p , for substances to be heated.

Introduction

In the search for a relevant and scientifically sound - as well as easy to apply - energy recovery criterion within the "Packaging and the environment/Energy recovery" working group (CEN/TC 261/SC 4/WG 4), the idea of using the adiabatic combustion temperature as an energy recovery criterion for packaging was brought forward. It was supported by Ref. 1. Here combustion was supposed to occur if :

$$ICV = V \cdot C \cdot t$$

where ICV is the net heat of combustion, or net calorific value, V is the flue gas volume, C the specific heat capacity of the gas, and t temperature. By relating t to a final temperature known to result in (fairly) complete (i.e., "environmentally friendly") combustion and then calculate the amount of heat needed to arrive at an adiabatic stage thus defined (the oxygen excess in the flue gas has to be chosen also), the adiabatic energy recovery criterion had come into being. Thus, the method could be described as an inverted adiabatic final temperature calculation.

Packaging material

A packaging, P , may consist of a single constituent, K , e.g., polyethylene (PE), or of two or more constituents. Let us consider the case of n constituents :

$$P = \{K_1, K_2, \dots, K_n\}$$

For example, if $P = \text{cardboard}$,

then $K_1 = \text{cellulose}$;
 $K_2 = \text{lignin}$;
 $K_3 = \text{filler material}$;
 $K_4 = \text{moisture, i.e., H}_2\text{O(l)}$.

Heat of combustion

If the heat of reaction of all the constituents, Q_i , is known, then an accurate enough value of the resulting heat of combustion of P , Q_p , is obtained by linear combination based on known fractions, f_i , of the constituents :

$$Q(P) = f_1 Q_1 + f_2 Q_2 + \dots + f_n Q_n$$

or

$$Q(P) = \sum_{i=1}^n f_i Q_i \quad (1)$$

If the heat of reaction is given as unit energy per unit mass, then f_i stands for mass fraction, w_i . If molar units are used, then f_i should be replaced by the mole fraction, x_i . However, since mole is an inconvenient unit substance for a compound material, calculations with Equation 1 will, in practice, be made with its specific (per unit mass) form¹ :

$$Q(P) / J \cdot g^{-1} = \sum_{i=1}^n f_i Q_i / J \cdot g^{-1}$$

The molar form is :

$$H_a(P) / J \cdot mol^{-1} = \sum_{i=1}^n x_i \Delta H_i / J \cdot mol^{-1}$$

In the case of heat recovery from packaging, Q_p and $Q_{net,i}$ are net values (net heat of combustion/net calorific value), Q_{net} (the index will most of the time be omitted in the following), which means that any water formed by the combustion process² is gaseous, $H_2O(g)$.

The flue gas final state

Primarily, the heat released in the combustor when P burns is used for heating the process products - as well as residual nitrogen and oxygen (excess air) and inert constituents present in P - from the ambient temperature, T_o , to the temperature of the flue gas (which has just left the flame zone). Even if the temperature of slag and bottom ash in reality is lower than the temperature of the flue gas, we stipulate that all post-combustion substances shall attain

¹ It is recommended that heat of combustion should be denoted Q and refer to unit mass (g), while enthalpy of combustion should be denoted ΔH and refer to unit substance = element/compound (mole) : $Q \cdot M = -\Delta H$, where M denotes the molar mass (g/mol) of the substance. Note that "heat" and "enthalpy" have different signs.

² *Process* includes the combustion reaction proper and any other reaction going on at the same time, e.g., dissociation reactions. The Q values refer to dry material, which means that evaporated moisture has to be excluded ; it is taken care of by being regarded as a separate constituent with its own Q value. It might be added in this connection that as far as the proposed CEN energy recovery criterion is concerned, moisture in the combustion air is excluded, i.e., the calculations are made under the assumption that the air is dry.

the same final temperature. The lower Q_P , the lower this final (not flame) temperature (which is further lowered by heat loss).

For purpose of the CEN energy recovery criterion, the required flue gas temperature is defined as the *adiabatic final temperature*, T_a , which is the calculated (theoretical) temperature that would be attained in a perfectly insulated, i.e., ideal combustor (no heat loss). Furthermore, T_a is chosen as the value specified in various EC directives on combustion plants. The current value for municipal solid waste incineration is $T_a = 850^\circ\text{C} = 1123\text{ K}$; Article 6 :2 in "Draft Directive Incineration of Waste", dated 1994-08-20. This draft (which in 1998 is intended to replace Directives 89/369/EEC from 8 June 1989 and 89/429/EEC from 21 June 1989 on new and existing, respectively, municipal waste incinerators) runs :

All incineration plants shall be designed, equipped and operated in such a way that the gas resulting from the combustion of the waste is raised, after the last injection of combustion air, in a controlled and homogeneous fashion and even under the most unfavourable conditions, to a temperature of at least 850°C, as measured at the inner wall of the combustion chamber, for at least two seconds in the presence of at least 6 % oxygen.

Though not explicitly stated in the directives, it should be obvious that 6 % O_2 refers to wet flue gas.

Article 7 : 4 in "Proposal for a Council Directive on the Incineration of Hazardous Waste", 92/C130/021, reads similarly, but with the addition that if halogenated organic substances are present, then $T_a \geq 1200^\circ\text{C}$. The minimum value of the oxygen content, $x_{\text{O}_2} = 0.06$, is also needed for criterion calculations, since it determines the air factor, λ .

Calorific gain (ΔQ)

The adiabatic final state being specified, the amount of heat required for attaining $T_a = 850^\circ\text{C}$ at 6 % O_2 , H_a (index *a* for *adiabatic*; the index will be omitted henceforth) can be calculated, provided the isobaric specific or molar heat capacity, C_p (this index will also be omitted), of all the substances are known for the temperature interval $T_o - T_a$. Even if C is fairly independent of the pressure (see, e.g. Ref 2) a pressure of 1 atm = 1,013 bar will be assumed.

The adiabatic amount of heat required for P can be calculated in analogy with Eq. 1 :

$$H(P) = \sum_{i=1}^n f_i H_i \quad (2)$$

or

$$H(P) / J \cdot g^{-1} = \sum_{i=1}^n w_i H_i / J \cdot g^{-1}$$

or

$$H(P) / J \cdot mol^{-1} = \sum_{i=1}^n x_i H_i / J \cdot mol^{-1}$$

If $Q(P) > H(P)$

or $Q(P) - H(P) > 0$

then there is - in our ideal system - sufficient heat to sustain combustion which is here defined as *calorific gain*, ΔQ :

$$\Delta Q = Q(P) - H(P) > 0 \quad (3)$$

Inserting Eq. 1 in Eq. 2 gives :

$$\Delta Q = \sum_{i=1}^n f_i (Q_i - H_i) \quad (4)$$

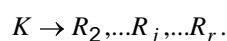
Thus, the minimum inferior calorific value can be defined as $Q_{i,\min} \equiv H_i$ and determined by calculating H_i .

Calculation of H_i

Post-combustion substances to be heated from T_o to T_a , where T_o , the ambient or room temperature, is chosen to be $25^\circ\text{C} = 298 \text{ K}$ (hand-book data usually refer to this temperature), are - or may be : combustion products, dissociation products, nitrogen, excess oxygen, and inerts.

Combustion products

A constituent that burns in air results in "r" products " R_j ", including oxygen (if $\lambda > 1$) and nitrogen :



In the treatment to follow, index 1 will be used for K , 2 for oxygen, 3 for water, 4 for carbon dioxide, and 5 for nitrogen. The adiabatic heat amount required by K per unit substance ($n_1 = 1 \text{ mole}$) or unit mass ($m_1 = 1 \text{ g}$) is :

$$H_K = \sum_{j=2}^r g_j \cdot C_j \Delta T \quad (5)$$

The factor g_j denotes the ratio of _the amount of R_j over the amount of burnt K . The (specific or molar) heat capacity, C , is the *mean value* between T_o and T_a , and $\Delta T = T_a - T_o = 825 \text{ K}$. The specific or molar heat capacity mean value is defined by :

$$\int_{T_o}^{T_a} C_j \cdot dT = C_j \Delta T \quad (6)$$

Having specified the temperature of the initial and final state, the corresponding integrals become constants as far as the adiabatic energy recovery criterion is concerned. The following values have been calculated by applying Simpson's equation to $C_i(T)$ data published - with the exception of CaO(s) - in Ref. 3. :

$$\int_{298}^{1123} C_{\text{CO}_2} \cdot dT = 27,0 \text{ kJ mol}^{-1} = 0,845 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{\text{N}_2} \cdot dT = 26,1 \text{ kJ mol}^{-1} = 0,931 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{\text{CO}_2} \cdot dT = 37,8 \text{ kJ mol}^{-1} = 0,858 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{\text{H}_2\text{O}} \cdot dT = 31,2 \text{ kJ mol}^{-1} = 1,73 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{\text{CaO}} \cdot dT = 40,7 \text{ kJ mol}^{-1} = 0,727 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{HCL} \cdot dT = 25,0 \text{ kJ mol}^{-1} = 0,686 \text{ kJ g}^{-1}$$

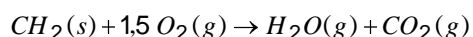
$$\int_{298}^{1123} C_{AL_2O_3} \cdot dT = 93,4 \text{ kJ mol}^{-1} = 0,916 \text{ kJ g}^{-1}$$

$$\int_{298}^{1123} C_{Fe_2O_3} \cdot dT = 115,6 \text{ kJ mol}^{-1} = 0,724 \text{ kJ g}^{-1}$$

The CaO -data were taken from Ref. 3. For inert fillers, like talc, mullite, etc., the value of the integral is, as a rule, 0,8 MJ kg^{-1} (cf. C_p -data for refractory materials given in Ref. 4).

EXAMPLE 1 K = Polyethylene foil.

Pure polyethylene, PE, (and polypropylene, PP) burns thus :



The following equations for the amounts of substance, n/mole, can be derived (for the mathematical chemistry behind, see Ref. 5. :

$$n_{O_2} \equiv n_2 = 1,5 n_1 \cdot (\lambda - 1) = g_2 \cdot n_1 \quad (7)$$

$$n_{H_2O} \equiv n_3 = n_1 = g_3 \cdot n_1 \quad (8)$$

$$n_{CO_2} \equiv n_4 = n_1 = g_4 \cdot n_1 \quad (9)$$

$$n_{N_2} \equiv n_5 = 5,66 n_1 \cdot \lambda \quad (10)$$

Addition of Eqs. 7 through 10 gives :

$$n_{tot} = n_1 (7,16 \lambda + 0,5) \quad (11)$$

Dividing Eq. 7 by Eq. 11 gives the oxygen mole fraction in the "wet" flue gas :

$$x_2 = 1,5 \cdot (\lambda - 1) / (7,16 \cdot \lambda + 0,5) \quad (12)$$

Putting $x_2 = 0,06$ in Eq. 12 gives $\lambda = 1,43$. Now the g-factors in Eqs. 7 through 10 can be computed : $g_2 = 0,644$, $g_3 = g_4 = 1$, $g_5 = 8,09$. Insertion into Eq. 5 gives :

$$H_{PE} = 0,644 C_2 \cdot \Delta T + C_3 \cdot \Delta T + C_4 \cdot \Delta T + 8,09 C_5 \cdot \Delta T \quad (13)$$

With molar units, we obtain :

$$H_{PE} / \text{kJ mol}^{-1} = 0,644 \cdot 27,0 + 1 \cdot 31,2 + 1 \cdot 37,8 + 8,09 \cdot 26,1 = 298$$

Dividing this value by the molar mass of PE, 14,03 g/mol, gives :

$$H_{PE} / \text{MJ kg}^{-1} = 21,2.$$

Dissociation products

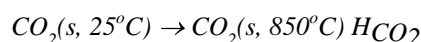
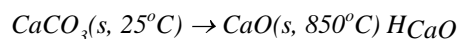
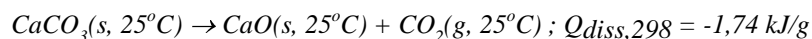
Dissociation is a type of reaction where an (endothermic) heat of reaction-term, Q_d , has to be added in Eq. 1³.

EXAMPLE 2K = Calcium carbonate

The dissociation of calcium carbonate, $CaCO_3$:



takes place at high temperature. By applying Hess' law, H_{CaCO_3} can be calculated thus :



Stoichiometry has it that 1g $CaCO_3$ gives 0,56 g CaO and 0,44 g CO_2 . With the mean specific heat capacities for CaO and CO_2 in the interval 25 - 850°C as derived from the JANAF-data (Ref. 3), we obtain :

$$Q_{diss, CaCO_3} / MJ \text{ kg}^{-1} = -1,74$$

$$H_{CaCO_3} / MJ \text{ kg}^{-1} = 0,56 \cdot 0,855 + 0,44 \cdot 1,009 = 0,92$$

And

$$\Delta Q = -1,74 - 0,92 = -2,7 \text{ MJ kg}^{-1}$$

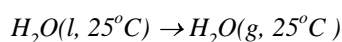
In molar units : $\Delta H_{diss} = -Q_{diss} \cdot M_{CaCO_3} = +1,74 \cdot 100,1 = 174 \text{ kJ / mol.}$

Evaporation products

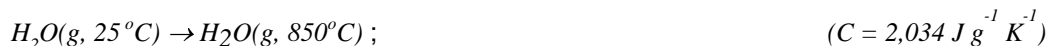
In this case there is no chemical reaction, only a phase change.

EXAMPLE 3 K = water

The calorific gain of moisture or water, $H_2O(l)$, can be calculated from heat of vaporization data and specific heat capacity data of $H_2O(l)$ and $H_2O(g)$:



$$Q_{vap,298} = -2,442 \text{ kJ g}^{-1}$$



$$H_{H_2O} / kJ \text{ g}^{-1} = 2,034 \cdot 10^{-3} \cdot 825 = 1,68$$

$$\Delta Q = -2,44 - 1,68 = -4,12 \text{ kJ g}^{-1}$$

³ It should be noted that heats of reaction other than heats of combustion - such as Q_d and Q_{vap} - have to be included in the Q(P)- term in order to match the corresponding experimental value.

The specific heat capacity of $H_2O(l)$, and Q_{vap} -data were obtained from Ref. 6.

Inert substances

An inert substance, typically a filler material, is just heated from T_o to T_a :

$$H_K / MJ kg^{-1} = (C_K / J g^{-1} K^{-1}) (\Delta T / K) \cdot 10^{-3} \quad (16)$$

EXAMPLE 4 $K =$ mullite

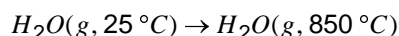
For mullite or aluminium silicate, $Al_2O_3 \cdot SiO_2$, and for lots of other fillers too :

$$C = 1 J g^{-1} K^{-1} \quad (Ref 7)$$

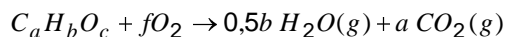
Thus : $H_{mullite} / MJ kg^{-1} = 1 \cdot 0,825 = 0,8$.

Air moisture

Even if we choose to stipulate dry air for the imaginary combustion of P in our ideal, adiabatic furnace, a study on its true effect on $H(P)$ is worthwhile. The calculation procedure will be the same as for inert substances (Eq. 16) and be based on the process :



The difference lies in the fact that moisture in the combustion air is not a constituent (K) of P , and that the H -value becomes a function of λ , which in turn depends on the chemical composition of the combustible constituents. For a fuel consisting of carbon, C , hydrogen, H , and oxygen, O , we have :



$$\text{Initial state, } S_o : \quad n_1 \quad n_{20} \quad n_{30} \quad 0 \quad \text{moles}$$

$$\text{Final state, } S_\infty : \quad n_1 \quad n_2 \quad n_3 \quad n_4 \quad \text{moles}$$

Thus, a term representing the amount of moisture entering the furnace with the air, n_{30} , has to be introduced. From the relations :

$$n_{20} = f\lambda \cdot n_{10} \quad \text{and} \quad n_{air} = 4,773 \cdot n_{20} = 4,773 \cdot n_{20} = f\lambda \cdot n_{20}$$

where n_{air} is the molar amount of dry air, the following equation can be derived :

$$n_{30} = 4,773 \cdot (x_{30} / (1 - x_{30})) \cdot f\lambda \cdot n_{10} \quad (17)$$

where x_{30} is the mole fraction of water vapour in the (moist) air. As can be read in a Mollier diagram, air of 50 % relative humidity contains 0,016 g vapour per g of dry air, which translates into $x_{30} = 0,026$ (i.e., 2,6 % by volume). Applying Eq. 17 to the burning of PE (see Example 1) in air of 50 % relative humidity gives :

$$n_{30} = 4,773 \cdot (0,026 / (1 - 0,026)) \cdot 1,5 \cdot 1,43 \cdot 1 = 0,27 \text{ moles/mole of PE.}$$

Finally, Equation. 16 gives $H_{30} = 0,58 MJ kg^{-1}$, which is only 0,2 % of H_{PE} when PE is burnt in dry air. So, the difference between the ideal, i.e. the standardised value of H and the real value referring to burning in moist air is negligible and lies within the uncertainty limits.

Some conclusions

Air nitrogen contributes a great deal to the H_i -value of combustible constituents.

Data for common packaging materials is given in Table 2.

For a typical beverage packaging laminate material (60 % cellulose, 7 % lignin, 6 % moisture, 8 % inert filler, and 19 % PE), the contribution to the HP-value from the different constituents is : Cellulose 50 %, lignin 9 %, moisture 1 %, inert filler 0,7 %, and PE 40 %, i.e., the combustible materials account for 98 %, moisture and inert filler for about 1 % each.

Table 2 - Data for some packaging material constituents for adiabatic energy recovery criterion calculations valid for wet flue gas, as appropriate.

Constituent i	monomer /reaction	Q_i (MJ kg ⁻¹)	$H_{a,i}$ (MJ kg ⁻¹)	$Q_{net,i} - H_{a,i}$ (MJ kg ⁻¹)	Ref.
Cellulose	$C_6H_{10}O_5$	16,1	7,9	8,2	8
Lignin	$C_{10}H_{12}O_{3,3}$	26 (softwood)	12	14	9
Starch	$C_6H_{10}O_5$	16,1	7,9	8,2	8
PC, polycarbonate	$C_{14}H_{14}O_3$	29	14	15	10
PE, polyethylene	CH_2	43	21	22	11
PP, polypropylene	CH_2	44,0	20,4	23,6	11
PS, polystyrene	C_8H_8	40,0	18,2	21,8	11
PET, polyethyleneterephthalate	$C_{10}H_8 O_4$	22		12	12
PLA, polylactide	$C_2H_2O_2$	11	6	5	13
PVC, polyvinyl chloride	C_2H_3Cl	17	8	9	11
Aluminium	$Al \rightarrow \alpha Al_2O_3$	31,0	6,4	24,6	3
Steel	$Fe \rightarrow Fe_2O_3$	0	0,4	-0,4	3
Water, moisture	H_2O	-2,44	1,68	-4,1	14
Inert filler	<i>e.g., talc</i>	-	0,8	-0,8	7
Instable filler	$CaCO_3 \rightarrow CaO$	-1,74	1	-3	15

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