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TNO-report

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The calorific value as a criterion for waste Recovery in the cement industry

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Executive summary

When accepting waste materials as substitutes for raw materials and/or fuels in the cement production process, it is important to evaluate the contribution of the waste to the process. An evaluation tool that TNO developed earlier for this purpose for Holcim is the MEP method.

In the MEP method, the chemical composition of the waste is used to distinguish a materials fraction from an energy fraction, after which the contributions of these fractions to the process are evaluated separately. As this is a rather complicated procedure, Holcim has asked TNO whether a minimum heating value could also be used as a reasonable alternative to the MEP method. This report evaluates the correctness of this supposition.

Holcim has suggested to formulate a waste recovery criterion based on the higher heating value on dry basis. However, the relationship between this parameter and the actual flame temperature is weak, mainly as a result of moisture that may be contained in waste and that lower the actual amount of energy available for the process. In addition, latent heat contained in produced water vapour is not being recovered in the cement production process. For these reasons, TNO is the opinion that a criterion based on the higher heating value does not reflect what is happening in the cement kiln. If a waste recovery criterion should be based on any heating value, the lower heating value on a wet basis would be most appropriate.

The analysis in this report shows a relation between the minimum combustion temperature that can be achieved in the cement production process and the lower heating value of a waste, depending on the process conditions in the kiln and actual heat losses from the flame. Based on such process data, a recovery criterion can be formulated for the lower heating value of waste in a specific kiln. Under typical process conditions (25% total process heat loss in the kiln and heat exchanger, from which 8% at the flame), a minimum Lower Heating Value of approximately 8 MJ/kg_{wet} is required to achieve a combustion temperature of 1500°C.

However, if the lower heating value does not exceed this criterion, one may still speak of a recovery operation in case the waste contains significant amounts of useful ash that may substitute raw materials. In case of doubt, it is advised to apply the existing MEP-method.

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1. Introduction

The use of wastes in the cement production process can be interesting for two main reasons:

- Natural mineral resources may be substituted if these minerals are also contained in the ash component of the waste.
- Fossil fuels may be substituted in case the autonomous incineration of the waste under the process conditions occurs at a sufficiently high combustion temperature.

In 1996, TNO developed the Materials and Energy Potential (MEP) method for Holcim to distinguish between waste elimination and waste recovery in the cement industry. This differentiation is not only important for a process manager when considering the acceptation of waste, but also as a regulatory tool. For instance, directives of the European Union allow the export of waste for the purpose of valorisation. With the MEP method, both of the above contributing factors are evaluated using the chemical composition of the waste to find the total contribution to the process.

A complicating factor hindering the practical, user-friendly application is that one always needs to calculate the combustion temperatures from the composition of the materials considered. Therefore, the development of quantitative criteria for waste recovery continued in the direction of a minimum LHV for materials taking into account the (useful) ash content.

Based on the MEP method and other studies, “Holcim” has suggested that a minimum HHV of 8 MJ/kg dry waste could be used as an alternative criterion for waste recovery in the cement industry and other industrial plants. TNO MEP was asked to evaluate from a theoretic perspective if a minimum heating value could serve as a suitable criterion for waste recovery. This report shows the results of this analysis.

2. The MEP method

The Materials and Energy Potential (MEP) method is a quantitative method to distinguish between waste recovery and elimination waste under prevailing process conditions in a cement kiln or other processes. While many other evaluation methods are solely based on the use of the waste as a fuel (the energy component), the MEP method regards the contribution of useful ash components separately from the energy contribution. The following steps are taken in this evaluation process:

1. A division is made between the raw materials fraction and the remainder part of the waste that is separately evaluated as a source of energy
2. Both the raw materials and the energy contributions of the waste are expressed quantitatively. In this assessment, the process conditions need to be provided.
3. The use of waste is assessed as a recovery or elimination operation.

2.1 The materials contribution

The MEP method quantifies the materials and energy contribution of the added waste to the process under predefined conditions in dimensionless numbers M and E for the materials fraction and the energy fraction.

In this analysis, the waste is separated into a virtual materials fraction and an energy fraction. The materials fraction contains the components in the waste that contribute to the cement process, such as $CaO(CaCO_3)$, SiO_2, Al_2O3, Fe_2O_3 and SO_3. Water in the waste is allocated to the materials fraction of the waste up to a maximum limit that also applies to the raw materials. Inert components in the waste are allocated to the materials fraction up to a maximum of the limit that also applies to the raw materials. The maximum allowable water and inert fractions depend mainly on the process (wet or dry cement production). The raw materials fraction M is then defined as

$$M = \frac{usmf}{\left(1-\min\left(waf, mwaf\right)\right)\left(1-\min\left(inf, maif\right)\right)}$$

where

$usmf$ = fraction of useful materials in waste as such

waf = fraction of water in waste as such

$mwaf$ = maximum water fraction allowed in the raw materials fraction

$\min(waf,mwaf)$ = water fraction in waste, up to what is normally allowed in the raw materials fraction

inf = fraction of inert, non-functional components in the waste

$maif$ = maximum allowable inert fraction in raw materials fraction

$\min(waf,mwaf)$ = fraction of inert, non-functional components found in waste, up to what is normally allowed in the raw materials fraction

It follows that for M = 1, the waste substitutes raw materials on a 1:1 ratio.

2.2 The energy contribution

In the MEP method, the energy fraction of the waste is attributed to the remaining waste material that excludes the useful minerals and (part of) the moisture and inert component, depending on the process conditions. The measure E expresses how capable this virtual fuel is to achieve a reference temperature T_{ref} in the process under the prevailing process conditions, starting from an initial temperature T_0:

$$E = \frac{(T_{comb} - T_0)}{(T_{ref} - T_0)}$$

For example, for the process of clincker formation in the cement kiln, a clincker temperature level of 1450°C is minimally required, therefore one can assume that the combustion temperature should be at least 1500 °C. If preheated air at 800°C is regarded as the reference temperature, the measure E is calculated as

$$E = \frac{(T_{comb} - 800)}{(1500 - 800)}$$

If follows that for E=1, the energy fraction in the waste contributes to the process and can be regarded as recovery operation.

2.3 Fuel recovery or elimination

While the processing of waste in the cement manufacturing process can surely be regarded as a recovery operation if only M= 1 or E=1, the MEP methods combines these two measures in the criterion for recovery: $E + M \geq 1$. This is illustrated below for a number of fuels in the wet- and dry cement process:

	Organic solvent	**Filtration earth**	**Artificial waste**	**Filter cake**	**LD slag**
LHV as such (MJ/kg$_w$)	25	12.5	3.4	6	0
Water (% as such)	20	20	50	50	5
Ash (% as such)	0	50	20	20	95
Dry cement process (mwaf=0.15, maif = 0.10, T_{ref}=1500°C, T_0=800°C)					
T_{comb} of energy fraction	1873	1912	1151	1400	NA
M	0.00	0.59	0.24	0.24	1.00
E	1.53	1.75	0.50	0.86	0.00
E+M	1.53	2.45	0.74	1.09	1.00
Valorisation?	yes	yes	no	yes	yes
Wet cement process (mwaf=0.30, maif = 0.10, T_{ref}=1500°C, T_0=800°C)					
T_{comb} of energy fraction	1873	2023	1212	1476	NA
M	0.00	0.70	0.29	0.29	1.00
E	1.53	1.75	0.59	0.96	0.00
E+M	1.53	2.45	0.88	1.25	1.00
Valorisation?	yes	yes	no	yes	yes

3. LHV as a criterion for waste recovery in cement production

A major disadvantage of the MEP method is the necessity to calculate the combustion temperature under actual process conditions from the composition of the materials considered. Therefore, the development of quantitative criteria for waste recovery continued in the direction of a minimum heating value for materials taking into account the (useful) ash content.

Based on the MEP method and other studies, “Holcim” has proposed a minimum HHV of 8 MJ/kg on a dry basis for waste recovery in the cement industry and other industrial plants. In section 3.1 however, it is argued that the LHV on a wet basis could serve as a more appropriate basis for such criterion than the suggested HHV on a dry basis. Further, the usefulness of a minimum lower heating value on wet basis will be evaluated as a criterion for recovery or elimination of waste as a fuel.

The relation between the heating value of waste and the combustion temperature when incinerated under typical process conditions in a cement kiln has been analysed in a five-step approach:

1. The relation between LHV and combustion temperature is evaluated for dry and ash free fuels containing only carbon, hydrogen and oxygen.
2. The results of (1) are verified with actual fuels, excluding ash and moisture.
3. The influence of ash and moisture is evaluated
4. A general criterion for a minimum LHV for the cement process is provided.

In sections 3.2 and 3.3, the calculation procedures of LHV and combustion temperature are explained. Then, the relationship between both parameters is analysed according to the above approach.

3.1 Selection of heating value as a criterion for waste recovery

While the higher heating value (HHV) of a fuel describes the amount of heat that can be used if a fuel is combusted and all water vapour in the combustion gases is fully condensed, the lower heating value of a fuel (LHV) describes the amount of heat available if the latent heat included in water vapour cannot be used by the process. The latter is the case in the cement production process; therefore this value provides the most useful indicator for the energy content of fuels and is proposed by the authors as the most appropriate indicator to base an evaluation upon.

Further, it is most appropriate to use the LHV of the fuel on a wet basis, since moisture results in less net energy input to the combustion process as well as a lower combustion temperature.

3.2 Calculation of the LHV of a fuel

The lower heating value on a wet basis can be estimated from the chemical composition, as is illustrated in Mitchells equation:

$$LHV_{wb} = LHV_{daf} \times \left(1 - X_{ash,\,db}\right) \times \left(1 - mc_{wb}\right)$$

where

$$LHV_{daf} = \left(34X_{C,db} + 102X_{H,db} - 9.8X_{O,db} + 4.5X_{N,db} + 19.1X_{S,db}\right)\left(1 - mc_{wb}\right) - 2.5mc_{wb}$$

In the above equations, the following notations are used:
LHV_{wb} = lower heating value on a wet basis
LHV_{daf} = lower heating value on a dry and ash-free basis
$X_{ash,db}$ = ash fraction on a dry basis
mc_{wb} = moisture content on a wet basis
$X_{C,\,db}$ = carbon contents of the fuel on a dry basis
$X_{H,\,db}$ = hydrogen contents of the fuel on a dry basis
$X_{O,\,db}$ = oxygen contents of the fuel on a dry basis
$X_{N,\,db}$ = nitrogen contents of the fuel on a dry basis
$X_{S,\,db}$ = sulphur contents of the fuel on a dry basis

For the far majority of fuels, nitrogen and sulphur concentrations are relatively low as compared to carbon, hydrogen and oxygen. As a result, carbon and hydrogen are main contributors to the energy value of a fuel, whereas sulphur and nitrogen usually contribute relatively little.

In case of a dry fuel with no ash, $X_{C,db} + X_{H,db} + X_{O,db}$ add up to almost 1, and the above equation can be approached by

$$LHV_{daf} = 34X_{C,db} + 102X_{H,db} - 9.8X_{O,db}$$

It can be shown that for any dry and ash-free fuel, approximately 2,45 mol of oxygen is required to generate 1 MJ of heat under stoichiometric combustion conditions in practise. The amount of combustion air needed to generate a given thermal power output is therefore almost independent of the type of fuel used.

In practise, almost any fuel contains moisture and ash. This can reduce the LHV significantly.

3.3 Calculation of the combustion temperature of a fuel

The combustion temperature that can be achieved with a specified fuel depends on many factors. Basically, the reaction enthalpy of combustion is used to heat up the fuel, combustion products and excess air to the combustion temperature. Amongst others, one needs to involve the c_p-values of the gases, which are temperature dependent as well. This calculation is not straightforward but has to be done through an iteration procedure.

In practise, the following factors are needed to obtain the combustion temperature of a fuel in a combustion process:

1. the chemical composition of the fuel, including ash and moisture content. While carbon and hydrogen increase the combustion temperature, ash and moisture contained in the fuel have a lowering effect.
2. the temperature of the fuel at starting conditions
   A warmer fuel results in a slightly higher combustion temperature.
3. the c_p values of the fuel and the ash component of the fuel.
   The energy required for heating fuel and ash is proportional to the c_p-values.
4. the excess air ratio or the oxygen percentage in the dry flue gases.
   The amount of combustion air required depends on the chemical composition of the fuel and the excess air ratio required for complete combustion. Air contains approx. 80% nitrogen, which also has to be heated up to the combustion temperature.
5. the humidity and temperature of the combustion air used
   pre-heated combustion air leads to a higher combustion temperature, humid combustion air results in a lower combustion temperature.
6. eventual energy losses experienced during combustion. Heat is transferred by conduction through the walls of a cement kiln, leading to a lower combustion temperature.

3.4 Observations from real fuels

It has been shown in section 3.3 that moisture and ash contained in waste lower both the combustion temperature as well as the lower heating value of the waste. For this reason, it is most accurate to split the waste into an energy component and a materials component, as is done in the MEP method. However, the easiest way to judge the contribution of a waste material to the cement production process is by comparing the measured lower heating value of the integral waste with a reference criterion for the integral waste, without dividing the waste into both fractions.

In this section, it is examined if the variations in LHV caused by the presence of ash and moisture in real waste, would make such a recovery criterion based on the LHV of the integral waste acceptable or not.

Figure 3.1 shows the relationship between the combustion temperature of the energy component of different types of waste in a cement kiln and the LHV of the integral waste. One can be observe that the combustion temperature of the non-material component generally increases with the lower heating value of the total waste. However, it does not provide enough ground to agree on a cut-off criterion since the influence of ash and moisture is not yet clear.

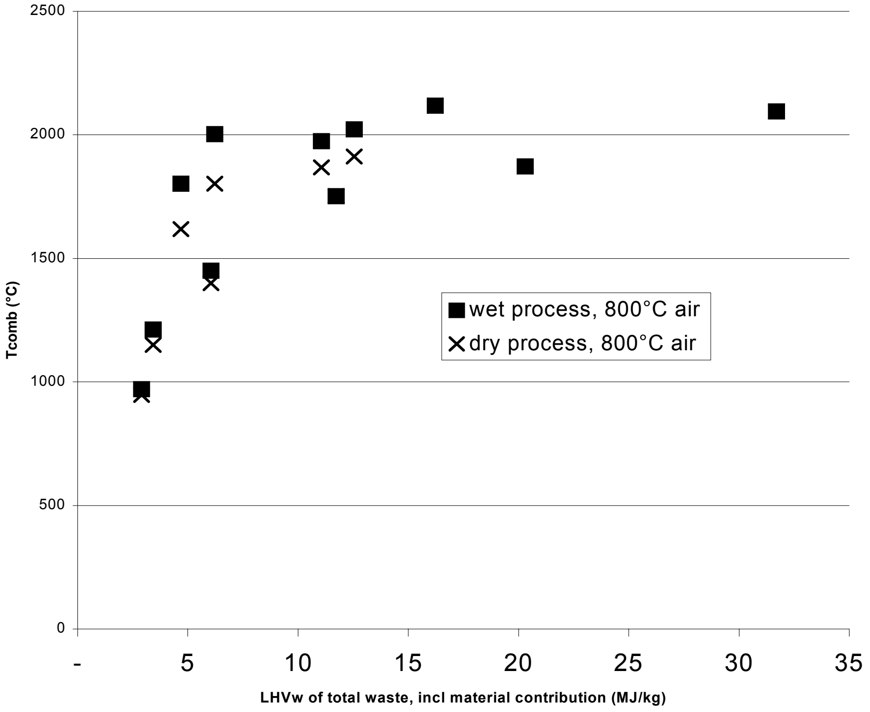

Figure 3.1 *Combustion temperature of the energy (non-material) part of different types of waste as function of Lower Heating Value of the integral waste. The energy component remains after subtraction of the material component (process conditions: T_{air}=800°C, 3% O_2, 25% heat losses assumed).*

Figure 3.2 shows the same relation, but now with the lower heating value of the energy component of the same types of waste on the horizontal axis. Though a waste recovery criterion based on the energy component of waste is not very practical, it can be seen that the variation of data around the average curve is much less than in Figure 3.1. It is clear that any criterion based on the lower heating value of the full waste will be less reliable than a criterion based on the energy component.

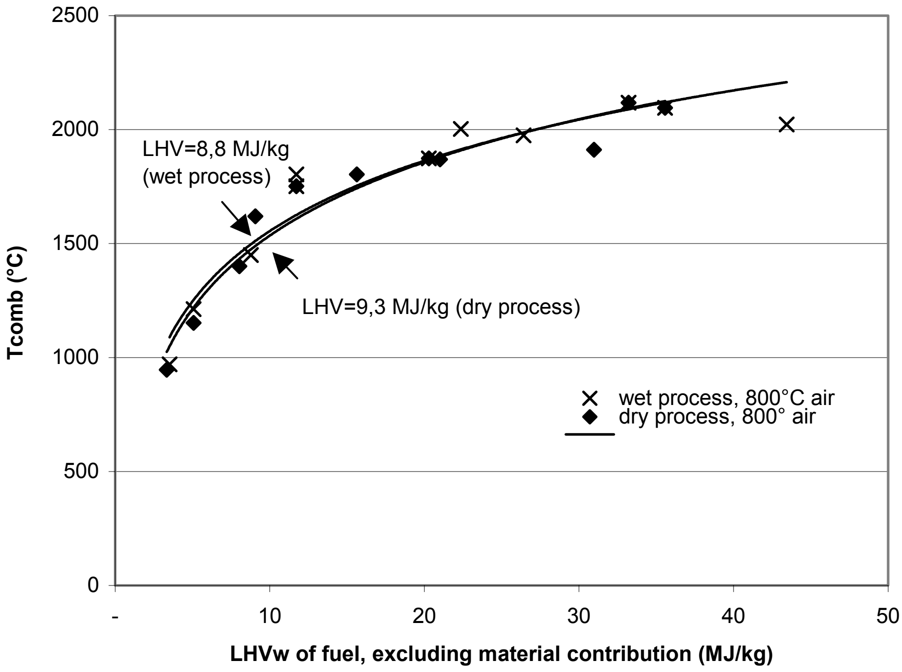

Figure 3.2 *Combustion temperature as function of Lower Heating Value of the energy component of different wastes. The energy component remains after substraction of the material component (process conditions: T_{air}=800°C, 3% O_2, 25% heat losses assumed).*

From this brief analysis it can be observed that there seems to be a relation between the two parameters that could be used as an indicator. Figure 3.2 shows that on the average, the energy part of a waste needs to have a minimum heating value of approximately 9 MJ/kg to achieve a combustion temperature of 1500°C. The data however still shows a significant spread and it is uncertain whether or not all types of waste are covered using such a criterion. For this reason, a more thorough analysis is presented in the next chapter.

4. Theoretical evaluation of the relationship between LHV and combustion temperature

4.1 The relation between LHV and combustion temperature for fuels without ash and moisture

The relation between LHV and combustion temperature is illustrated in Figure 4.1 for fuels that do not contain ash or moisture. For this diagram it has been assumed that the fuels solely consist of carbon, oxygen and hydrogen. In the same diagram, real fuels are shown on ash and moisture free basis. For all of these fuels, this sum adds up to at least 0.95. It can be shown that the effects of neglecting other fuel components on the outcome are negligible.

It can be observed that the combustion temperature for the dry and ash-free fuels shown varies between 2280 for biomass fuels to 2550 °C for coal, but there is no obvious relation with the calorific value. For different fuels with the same calorific value on a dry, ash free basis, the combustion temperature increases with carbon content. It was already shown in 3.1 that fuels with a higher carbon or hydrogen content (again dry and ash free) result in an increased lower heating value.

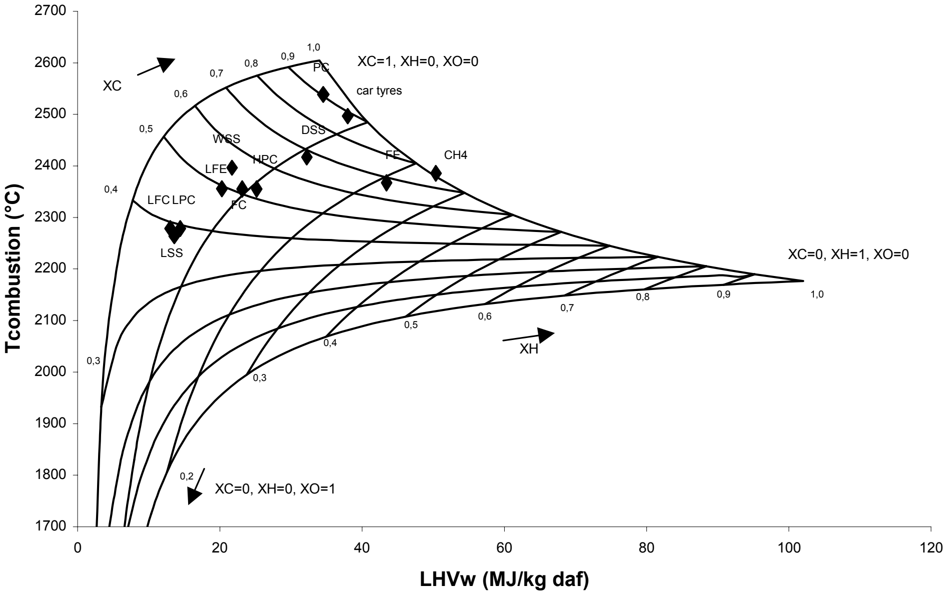

Figure 4.1 Combustion temperature of dry and ash free fuels in a cement kiln ($T_{combustion\ air}$ = 800°C, 3% O_2, no energy losses)

4.2 The influence of moisture on the relation between LHV and combustion temperature

In case all ash contained in a fuel contributes to the cement production process by substituting raw materials, it would be sufficient to analyse the T(LHV) relationship for the ashless component of a fuels, with moisture content as remaining variable. This chapter shows how this relationship appears for different fuels. In section 4.3, the influence of ash ballast on the conclusions drawn in this chapter are evaluated.

The below graph depicts the influence of moisture content on the relation between LHV and combustion temperature for different fuels with varying moisture content, assuming that ash is taken out to substitute raw material. It can be observed that these lines never cross one another. Typical process conditions are assumed (preheated air at 800°C, 3% O_2, no heat losses assumed).

For the formulation of a recovery criterion for fuels based on LHV, one should look at the lowest T(LHV) curve that is likely to occur. In the below graph, this case is obtained for gaseous fuels such as hydrogen and methane. However, a criterion based on these gaseous fuels is of no value, since the high moisture content that is necessary to achieve a combustion temperature under 1500 °C (80% for CH_4 and 90 % for hydrogen) is never achieved. One can therefore omit these fuels when formulating a criterion for fuel recovery.

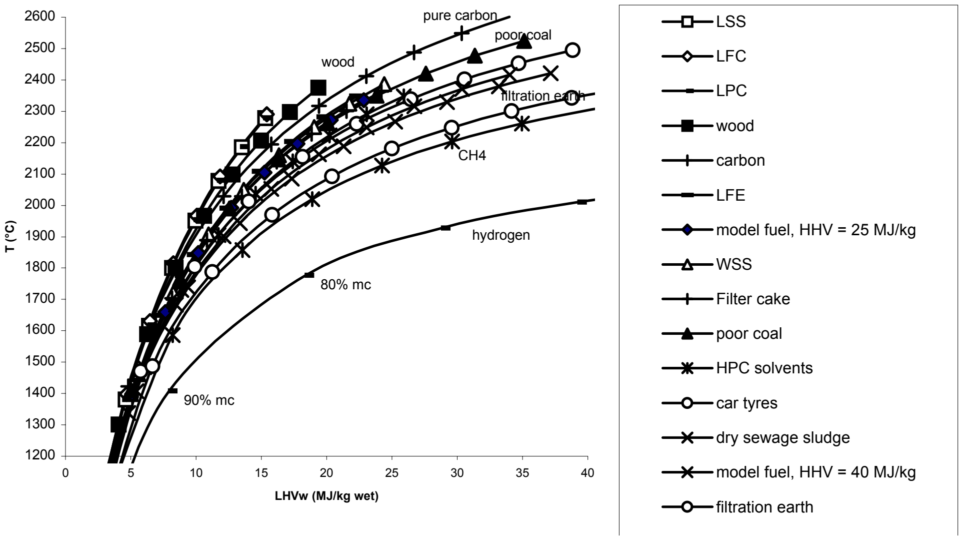

Figure 4.2 Combustion temperature of different fuels with varying moisture content, assuming that ash is excluded from the fuel. (T_{air}=800°C, 3% O_2, excluding heat losses). The legend shows the fuels ranked in order of combustion temperature, assuming the same LHV applies.

The composition of filtration earth results in one of the lowest T(LHV) curves possible. Figure 4.3 shows the same graph, but zoomed into the region where 1500 °C is achieved.

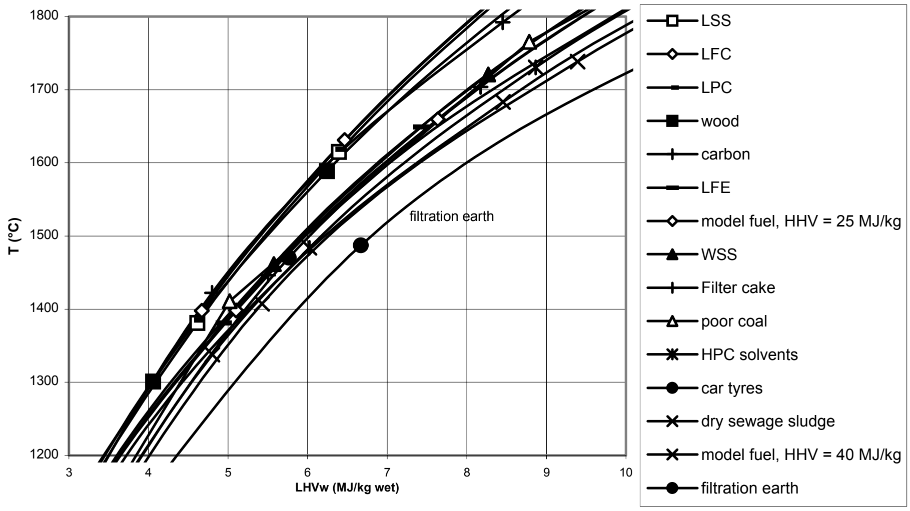

Figure 4.3 *Combustion temperature of different fuels with varying moisture content, assuming that ash is excluded from the fuel. (T_{air}=800°C, flue gas contains 3% O_2, heat losses in the process are excluded). The legend shows the fuels ranked in order of combustion temperature, assuming the same LHV applies.*

It can be concluded that a combustion temperature of 1500 °C is always achieved under the given process conditions if the LHV_w of the ashless fuel exceeds 6,8 MJ/kg. However, this conclusion is only valid in case one assumes that heat losses of the flame are negligible at the stadium where the fuel/combustion air mixture heats up. In practise however, the flame length may be approximately 40-50 meters, leading to significant heat transfer due to radiation to the clincker and the kiln walls. If heat losses of the flame are considerable, the combustion temperature of a fuel sinks significantly. This effect is shown in Figure 4.4 for filtration earth.

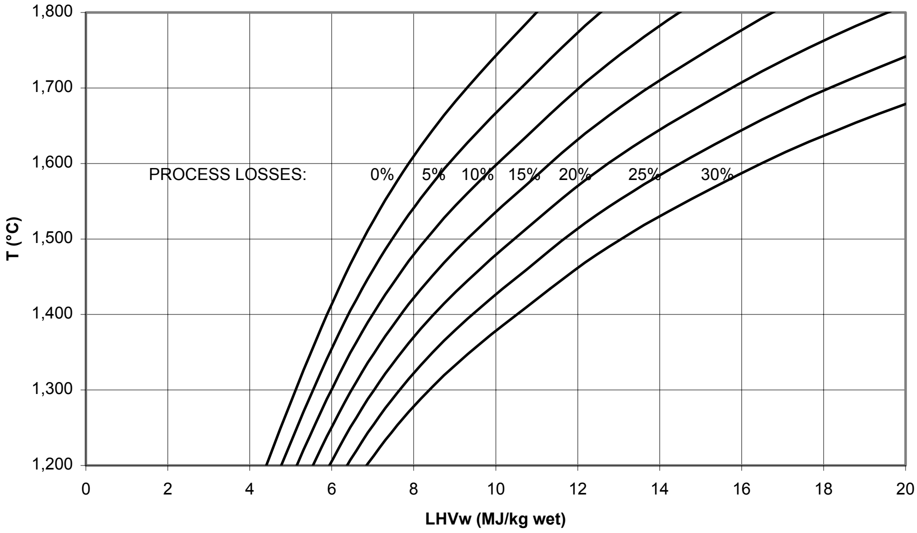

Figure 4.4 *The influence of flame heat losses on the combustion temperature of filtration earth. Each curve represents a constant flame heat loss, for ashless fuels with varying moisture content. Ash is excluded from the fuel. (T_{air}=800°C, flue gas contains 3% O_2,).*

Figure 4.4 shows that a recovery criterion for the LHV, based on the combustion temperature heavily depends on the heat losses of the flame in the kiln. A computer simulation model for cement kilns, developed by TNO, has been used to estimate the flame heat losses under typical process conditions. If it is assumed that flame heat losses are 8%, this results in a minimum LHV for ashless fuels of 8 MJ/kg_w to achieve a combustion temperature of 1500°C.

However, this criterion cannot be generalised and should be treated with great caution, since the actual flame heat losses may vary from case to case as a result of different operating temperatures and kiln configurations. can be used to estimate flame heat losses under actual process conditions. It is recommended that additional computer simulations are performed to evaluate the impact of different kiln configurations.

4.3 The influence of ash on the relation between LHV and combustion temperature for wet fuels

In 4.2, minimum lower heating values were proposed for wastes that do not contain ash. If all ash in a fuel substitutes raw material, it can be considered useful and these conclusions hold for the energy component of a waste material. In practise however, part of the ash contained in waste may not contribute to the process. If the amount of inert material in waste exceeds normal concentrations in raw material of the kiln, one should appoint the remaining inert to the energy component of the waste.

The effect of adding ash to a fuel is that both the combustion temperature and the heating value are lowered. This is illustrated below for filtration earth (other fuels show very similar graphs).

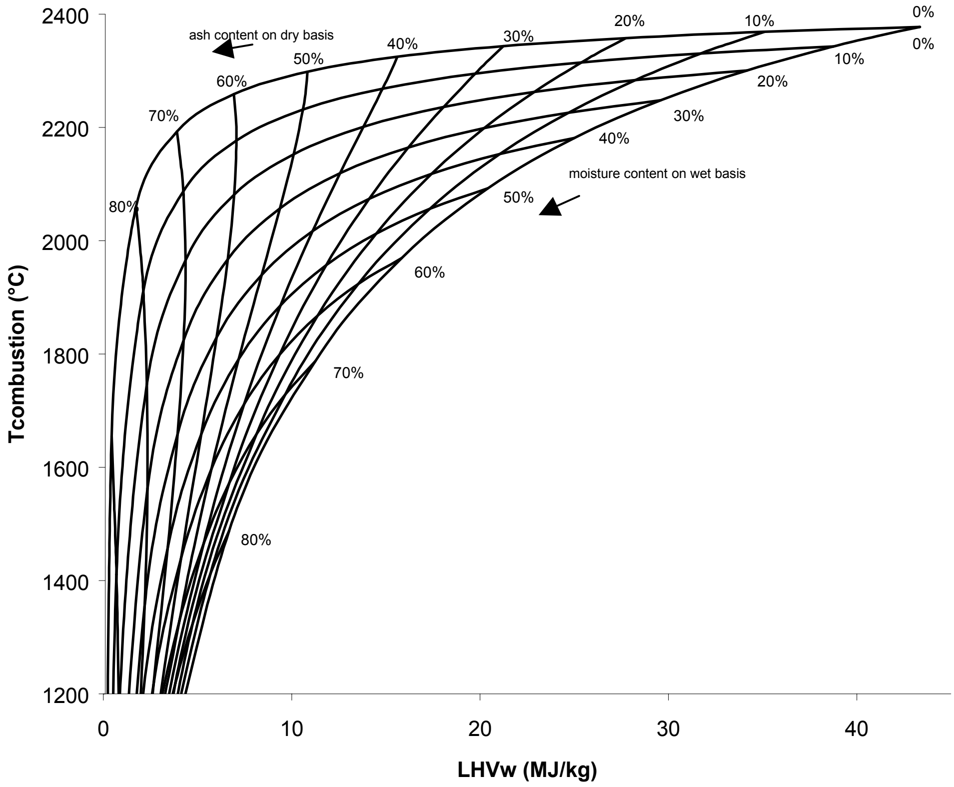

Figure 4.5 Combustion temperature of filtration earth with varying ash load and moisture content (T_{air}=800°C, 3% O_2, excluding heat losses)

Both the heating value and the combustion temperature decrease with increasing ash content of a fuel (this was also shown in 4.2 for the moisture content). However, since the mean c_p-value of ash in the heating trajectory is significantly lower than that the evaporation heat of water (approximately 1500 kJ/kg/K versus 2000 kJ/kg/K), adding ash to a dry, ashless fuel has less impact on the combustion temperature than adding moisture.

As a result of this observation, one can conclude that for any fuel, the most pessimistic guess for the combustion temperature with a given LHV occurs if one uses the T_{comb}(LHV) curve for an ash content of zero. In the above example of filtration earth (Figure 4.5), a process temperature of 1500°C is obtained under the given process conditions for any moisture and ash content if the LHV_w is at least equal to 6.8 MJ/kg_w. As was shown in Figure 4.2, this value also holds for other fuels[1]. If process losses are to be taken into account, this value increases to approx. 8 $MJ/kg_{w,}$ as was shown in Figure 4.4.

For other fuels, similar diagrams can be drawn. However, in all cases the line with zero ash content is the lowest line, since the c_p value of ash is lower than the evaporation heat of water.

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[1] Except for some theoretical fuels that do not occur in practice, consisting of gases with very high amounts of moisture or ash.

5. Conclusions

It is concluded that a reliable criterion can be formulated for a minimum heating value of the energy fraction of waste, if the chemical composition is known and the waste can be divided into an energy fraction and a waste fraction. Such a criterion could serve as alternative to the MEP method. The underlying study suggests that if process losses are neglected, the recovery criterion for a cement process with air preheating at 800°C and 3% O_2 in the flue gases should be that the energy fraction waste has a minimum lower heating value of approximately 7 MJ/kg_w on wet basis, for any common liquid or solid fuel, independent on ash and water content.

However, if 8% flame heat losses are taken into account, this criterion increases to approximately 8 MJ/kg_w. As the flame heat losses in the actual kiln determine this criterion to a large degree, it is advised to estimate these losses accurately, using computer simulation software.

It is not advised to base a recovery criterion on the Higher Heating Value on a dry basis, since eventual moisture contained in waste results in less energy input and a lower combustion temperature. The latent heat included in the HHV is not relevant since water vapour contained in the flue gases is not condensed before the chimney.

If the chemical composition of a waste is unknown, one could as well argue that the use of this waste in a cement kiln can be regarded as a recovery operation if the lower heating value of the integral waste exceeds the above criteria. However, this does not imply that the use of wastes with a heating value lower than the criterion should always be regarded as an elimination operation, since the material contribution (which is not taken into consideration in the ‘minimum heating value’ method) is then not taken into consideration.

A two-step approach can therefore be taken in the evaluation of the suitability of wastes for the cement process:

1. If the lower heating value of the integral waste already exceeds the above criteria, one could speak of a recovery operation as fuel.
2. If this is not the case, it is advised to determine the chemical composition and evaluate the contribution to the process using the existing MEP method.

6. Authentication

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-

Date upon which, or period in which, the research took place:

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