



The use of enzymes for beer brewing: Thermodynamic comparison on resource use



Laura H.G. van Donkelaar^a, Joost Mostert^a, Filippos K. Zisopoulos^{a, b}, Remko M. Boom^a, Atze-Jan van der Goot^{a, *}

^a Laboratory of Food Process Engineering, Wageningen University, Bornse Weilanden 9, 6708, WG, Wageningen, The Netherlands

^b Top Institute Food and Nutrition (TIFN), Nieuwe Kanaal 9A, 6709, PA, Wageningen, The Netherlands

ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form

3 July 2016

Accepted 3 September 2016

Available online 14 September 2016

Keywords:

Exergy

Enzymes

Brewing

Unmalted barley

Biotechnology

ABSTRACT

The exergetic performance of beer produced by the conventional malting and brewing process is compared with that of beer produced using an enzyme-assisted process. The aim is to estimate if the use of an exogenous enzyme formulation reduces the environmental impact of the overall brewing process. The exergy efficiency of malting was 77%. The main exergy losses stem from the use of natural gas for kilning and from starch loss during germination. The exergy efficiency of the enzyme production process ranges between 20% and 42% depending on if the by-product was considered useful. The main exergy loss was due to high power requirement for fermentation. The total exergy input in the enzyme production process was 30 times the standard chemical exergy of the enzyme, which makes it exergetically expensive. Nevertheless, the total exergy input for the production of 100 kg beer was larger for the conventional process (441 MJ) than for the enzyme-assisted process (354 MJ). Moreover, beer produced using enzymes reduced the use of water, raw materials and natural gas by 7%, 14% and 78% respectively. Consequently, the exergy loss in the enzyme production process is compensated by the prevention of exergy loss in the total beer brewing process.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Brewing is a traditional process, which can still be further optimized with respect to environmental impact [1]. Several sustainability analyses have been performed on the process [2–4] and studies have been aimed at the re-use or prevention of by-product streams to minimize water and raw material losses and energy use [5–9]. Even though it does not take into account every aspect of sustainability, exergy analysis is based on the second law of thermodynamics and, therefore, is considered as an objective method to compare material and energy losses occurring in a system both quantitatively and qualitatively [10]. As formulated by Szargut, exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of its surrounding nature by means of reversible processes, involving interaction only with the components of nature [11]. Exergy analysis has been used to analyse, optimize, and

compare various food processes and food production chains in terms of their resource use efficiency [12]. An improvement of the exergetic or thermodynamic efficiency of a process reflects a reduction on its overall use of resources and hence its environmental impact [13]. Exergy analysis can be applied to many different food production chains to identify improvements, and to compare the thermodynamic performance of existing processes to potential alternatives. This was done for example in vegetable oil (/and protein) production [14,15], in a fish-oil microencapsulation process [16], dairy processing [17], an isoflavone extraction process [18], and the use of plant based ingredients for fish feed [19] amongst others. The analysis shows if the use of an alternative process is in fact more efficient.

The outcome of an exergy analysis can be influenced by the system boundaries, which are chosen by the analyst, i.e. wider system boundaries imply a more complex but also a more complete analysis [20]. Besides, the allocation of the exergetic content of the streams will also influence the outcome of the analysis. In this paper, these aspects will be demonstrated when describing the exergetic production costs, or cumulative exergy consumption (CEXC), of enzymes.

* Corresponding author.

E-mail address: atzejan.vandergoot@wur.nl (A.-J. van der Goot).

Nomenclature/list of symbols

m	mass [kg]
x	mass fraction of component [–]
h	Enthalpy [kJ/mol]
Q	heat [kJ]
W	work performed by the system
Ex	exergy [kJ]
c_p	specific heat capacity [kJ/kg K]
T_0	reference temperature [K]
T	temperature [K]
R	ideal gas constant [kJ/mol K]
m_x	average molar mass of the stream [kg/mol]
P_0	reference pressure [Pa]
P	pressure [Pa]
b_0	standard chemical exergy [kJ/kg] for which the values can be found in Table 3
x_i	mass fraction of component i [–]

The conventional brewing process has 3 main process stages. The first stage is malting, during which enzymes are synthesized in the barley kernel. In this stage the endosperm is modified: cell walls are broken down to render the protein and starch inside the cells more accessible. The second stage is mashing, during this stage the enzymes hydrolyse starch into fermentable sugars and proteins into amino acids. The third stage is fermentation, during which yeast ferment the sugars into alcohol. Brewing with unmalted barley grains more attention because of the economic advantages and its potential for water and energy savings. Additionally, material losses due to respiration are prevented [21]. In this paper, we analyse the both beer brewing processes with exergy analysis.

A disadvantage of brewing with unmalted barley is the low amount of available endogenous enzymes present in the native kernel. Therefore the addition of enzyme formulations is necessary. These formulations usually contain a combination of α -amylase, pullulanase, proteases, lipase, β -glucanase, and xylanase. The effectiveness of these formulations has been investigated and documented in various reports. No negative effect on beer quality was found when 50% or up to 100% of the malt was replaced by unmalted barley [21–24].

One should take into account that the production of an enzyme formulation also requires resources and produces waste. This raises the question if the use of enzymes requires less resources compared to the malting process. In many studies the standard chemical exergy of purified ingredients like enzymes, protein isolates or other isolated or purified ingredients is used in exergetic assessments, neglecting the CExC of these components. The aim of this paper therefore is two-fold. It assesses the exergetic performance of traditional beer brewing by the conventional malting and brewing process, and compares it to an enzyme-assisted brewing process. It also estimates the CExC of the enzyme formulation used in the enzyme-assisted brewing process.

2. General description of the brewing production chain

To analyse the brewing process and the enzyme production process, we first defined the process operations of the process. Subsequently we did the mass flow analysis, then the energy analysis, and finally the exergy analysis.

2.1. System boundaries

In the brewing process, the malting process was taken into account when malt was used, while enzyme production was considered in the enzyme-assisted brewing process. The compositions of the various streams in both processes are listed in Table 1. The process configurations of the analysed processes are shown in Fig. 1. The production of the growth medium used in the enzyme production process is not considered in the analysis, which means that only the chemical exergy for the ingredients present in the medium was taken into account. The same counts for glycerol, as this product is currently produced as a by-product of biodiesel. All exergy input for this process was attributed to the biodiesel and not to the glycerol used in the enzyme formulation.

Data collection for every process step is usually quite cumbersome (e.g. because they are hard to measure, because they are not readily available or because they might be confidential etc.). Therefore we had to make several assumptions in order to calculate the exergy destruction in these processes. Some assumptions, like assuming an adiabatic process, are simplifying the situation, as heat losses do occur in reality. The data and assumptions made for the enzyme production process, malting process and brewing process and the associated references are listed in Table 2.

2.2. Exergy analysis

Mass and energy balances were calculated with Eq. (1) and Eq. (2).

$$\sum m_{in} - \sum m_{out} = 0 \quad (1)$$

$$\sum (mh)_{out} - \sum (mh)_{in} = Q - W \quad (2)$$

The exergy was categorised into the chemical exergy (Eq. (6)) (the chemical exergy relates to the actual chemical exergy of a flow or a stream based on its composition and difference in chemical potentials in relation to the environment of reference) and the physical exergy (Eq. (3)) composed of the thermal and pressure exergy (Eq. (4) and Eq. (5)). The exergy loss was defined as the difference between the total exergy input and the total exergy output (Eq. (7)), and consisted of both the wasted exergy (i.e. theoretically usable but lost to the environment) and destroyed exergy (irreversibly lost) (Eq. (8)). Exergy wasted could be any stream, material or immaterial, which contains exergy (useful work) that could be available but is wasted to the environment due to, e.g. inadequate heat insulation, or mismanagement (i.e. food losses and food waste). The universal efficiency is described as 1-exergy_destroyed/exergy_in. Chemical exergy is very important to consider in an exergy analysis of a food production chain simply because they are usually much larger than physical exergy flows [18,36]. The chemical exergy efficiency of a process chain was therefore defined as the total output chemical exergy over the total input exergy (Eq. (9)) (also known as the cumulative degree of perfection [37]). The rational exergy efficiency was defined as the useful chemical exergy output over the total exergy input (Eq. (10)). The two different definitions of exergy efficiency we provided have an allocation function in order to differentiate between the exergy outputs that are usually considered as useful, and the total exergy outputs of the chain. In this way it is possible to estimate the potential for improvement. Dry enzyme, malt and beer were considered useful exergy output. It was debatable whether the fertilizer and enzyme formulation are to be considered as useful; we will discuss this in the results section. The cumulative exergy consumption (CExC) is related to the total cumulative exergy

Table 1
Composition of process streams.

Component	Composition (%)							
	Growth medium ^a	Enzyme formulation ^b	Barley ^c	Malt ^d	Fertilizer ^e	Spent grains ^f	Beer	
							Conventional process	Enzyme assisted
Water	93	65.1	13	5	70	80	92.33	92.47
Protein	2.8	4.9	9.57	11.09	13.97	5.6	0.86	0.79
Carbohydrates	3.5		73.95	79.87	11.63	11.7	1.71	1.59
of which starch			75.7	74.7				
of which fibres			24.3	25.3		100	100	100
Fats			1.52	1.76		1.64	0	0.00
Ash	0.7		1.96	2.27	4.4	1.06	0.22	0.20
Glycerol		30						
Ethanol							5	5

^a [28].

^b Protein content of commercial enzyme formulation was measured by DUMAS (conversion factor 6.25).

^c We assumed these values based on our own measured values in combination with [29].

^d Calculated from barley compositions and assumptions on malting (Appendix III).

^e All water and dry matter that does not end up in the enzyme formulation stream will end up in the fertilizer stream.

^f [29].

consumed to produce a product (Eq (11)).

$$Ex_{physical} = Ex_{thermal} + Ex_{pressure} \quad (3)$$

$$Ex_{thermal} = m \cdot c_p \cdot \left[(T - T_0) - T_0 \cdot \ln\left(\frac{T}{T_0}\right) \right] \quad (4)$$

$$Ex_{pressure} = \frac{R \cdot T_0}{m_x} \cdot \left[\ln\left(\frac{P}{P_0}\right) \right] \quad (5)$$

$$Ex_{stchem} = m \cdot \sum_{i=1}^n (b_0 \cdot x_i) \quad (6)$$

$$Ex_{loss} = Ex_{in} - Ex_{out} \quad (7)$$

$$Ex_{loss} = Ex_{waste} + Ex_{destruction} \quad (8)$$

$$\text{Total chemical exergy efficiency} = \frac{\text{Total } Ex_{chem\ out}}{\text{Total } Ex_{chem\ in}} \quad (9)$$

$$\text{Useful chemical exergy efficiency} = \frac{\text{Useful } Ex_{chem\ out}}{\text{Total } Ex_{chem\ in}} \quad (10)$$

$$\text{Cumulative exergy consumption} = CExC = \sum Ex_{loss} \quad (11)$$

The standard molecular mass, chemical exergy and heat capacity of the components that we used in this manuscript are listed in Table 3.

Mass and energy flows were visualized by Sankey diagrams and exergy flows were visualized by Grassmann diagrams, using e!Sankey 3.1 (ifu Hamburg GmbH, Hamburg, Germany).

3. Results and discussion

Fig. 2 shows the mass flows in the conventional malting process. The malting process consists of a steeping step in which water is added. This water is partially taken up by the grains. After germination the malt is dried with hot air to evaporate this water again. At the end of the process rootlets are removed.

During germination, a small part of starch is lost due to respiration. Nevertheless, this raw material loss is one of the main disadvantages of the conventional malting process. Less starch left in

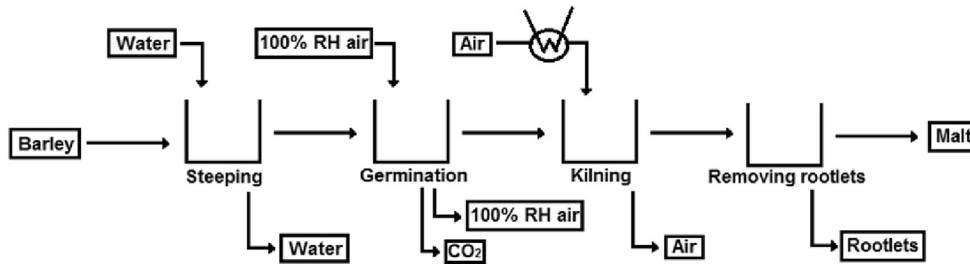
the malt means less starch is hydrolysed during brewing and therefore less beer is produced from the same amount of raw material. Another disadvantage is the required addition of water during steeping. About 456.5 kg of water is required during steeping and germination of 100 kg of malt. The water that is taken up has to be evaporated during kilning to ensure shelf life and facilitate transportation, requiring 537 MJ for kilning 100 kg malt. This value is in line with a study by Kribs et al. which reported an energy consumption of 500 MJ/100 kg malt for a conventional kilning process [25].

The Grassmann diagram in Fig. 3 shows the exergy flows of the conventional malting process. The process can be considered as exergy efficient (77%) since the destroyed exergy is relatively small compared to the (chemical) exergy of the main product stream. The total exergy loss for processing is 518 MJ/100 kg malt, of which 380 MJ is destroyed and 138 MJ is wasted. The main losses are due to the high quality energy (natural gas) used for removing water in the kilning process. In addition, about 7% dry matter is lost during malting due to respiration and the removal of rootlets.

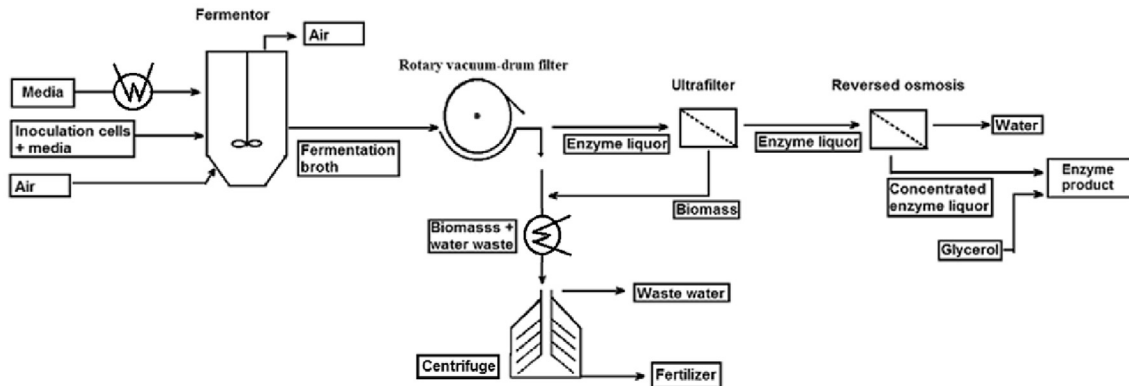
A potential alternative to malting is the use of unmalted barley in combination with exogenous enzymes [21]. The losses in the malting processes would be prevented, but materials and energy are needed to produce the enzyme mixture. Enzymes are produced in an industrial fermentation process in which yeast convert part of the protein present in a fermentation broth into enzymes. After fermentation, the enzymes are separated from the other biomass by a rotary vacuum drum filter. The biomass is sterilized, dried, and sold as a fertilizer. The enzyme liquor coming out of the drum filter is subsequently purified by ultrafiltration and concentrated by reverse osmosis. The enzyme liquor (7% protein, 93% water) is then mixed with glycerol to stabilize the enzyme solution that is the final product with a glycerol concentration of 30%.

Fig. 4 shows the main steps in the enzyme production process, which are: fermentation (including sterilisation of the medium and fermenter), recovery (including the concentration in the drum filter and the purification by ultrafilter and reverse osmosis), formulation (mixing the purified enzyme solution with glycerol), and waste treatment (including sterilisation and concentration). It was shown that aeration and cooling require most natural resources (air and water). The side stream can be considered either as a waste or as a useful by-product (e.g. fertilizer) [26]. Fig. 5 illustrates the exergy flows of the enzyme production process. The total exergy used in the production process of the enzyme is about 30 times the chemical exergy of the enzyme itself (676 MJ per kg dry enzyme).

A. Process flowchart of the conventional malting process



B. Process flowchart of the enzyme production process



C. Process flowchart of industrial brewing

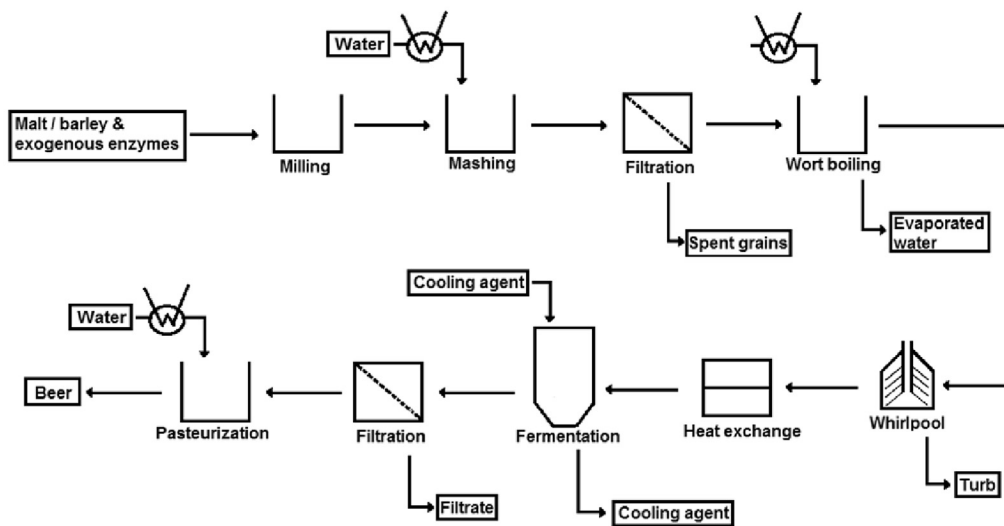


Fig. 1. Process flowchart of: A) the conventional malting process, B) the enzyme production process, C) the overall industrial brewing process.

Clearly, the exergy input of enzymes used in a process is considerably higher than their standard chemical exergy only. The CExC of these ingredients should be taken into account when assessing the thermodynamic performance of the overall system. The system boundaries affect the outcome of the exergy analysis and have to be extended to include the production of at least the purified ingredients (if not all raw materials).

The largest exergy destruction in the enzyme production process occurs during fermentation, due to the high power consumption of 2500 W m^3 . When calculating the exergy efficiency of

the process one has to decide how to attribute the loss of exergy to the produced products. The exergy efficiency of the total enzyme production process when the fertilizer stream is considered as a useful stream is 42%. However, when all exergy loss is allocated to the enzyme product, the efficiency of the process becomes 20% and even 3.4% when only the dry matter of the enzyme is considered. Here, we consider the enzymes as the main product of the process, making the fertilizer a side stream of this process. The selection of this side stream as a by-product or waste generated during the enzyme production process is arbitrary and, thus, debatable.

Table 2

General assumptions and assumptions per process and process unit.

General assumptions		
<ul style="list-style-type: none"> - Reference environment: $T_o = 283.25$ K, $P_o = 101.325$ kPa, RH = 82% (0.0064 kg moisture/kg dry air) - All processes are adiabatic (no heat losses to the environment) - Steam of 403.15 K and 2.7 bar was used for heating duties and produced from environmental water heated by natural gas (the embedded exergy in this water is 0) - Steam leaving the system was at 383.15 K and 1.4 bar - Environmental water was used for cooling - Cooling below 283.25 K was done by ammonia of 253.15 K (ammonia was reused so its standard chemical exergy was not taken into account) 		
Process unit	Assumptions	References
Assumptions malting process		
Steeping	<ul style="list-style-type: none"> - Dry matter loss during steeping is 1% (no compositional change) - The water used is 3.5 times the amount of barley 	[29] [29]
Germination	<ul style="list-style-type: none"> - 5.8% of the dry matter is lost due to respiration 	[29]
Kilning	<ul style="list-style-type: none"> - Kilning is done with hot air in 3 stages; drying to 23% moisture using air of 328.15 K (air out = 303.15 K), then to 12% moisture using air of 343.15 K (air out is increasing from 303.15 to 333.15 K) and finally to 5% moisture using air of 363.15 K (air out increasing to 353.15 K). - Germination happens at 290.15 K and 100% RH - The final moisture content of the malt is 5% w/w 	[30] [29] [29]
Cooling	<ul style="list-style-type: none"> - Cooling is done by outside air (RH = 18.2%) that heats up till 308.15 K 	[29]
Assumptions enzyme production process		
General	<ul style="list-style-type: none"> - All enzymes in the exogenous enzyme mixture for brewing are produced in a similar way 	[26,31,32]
Fermentation	<ul style="list-style-type: none"> - Sterilisation of the medium is at 394.15 K - Fermentation takes 6 days in a fed-batch stirred tank reactor at 303.15 K - The extracellular enzymes are produced by <i>Bacillus subtilis</i> (54 kg dm³) - Agitation takes 2500 W/m³ - Enzyme yield is 0.1 kg enzyme/kg substrate - Cooling water of the sterilized medium leaves at 368.15 K 	[26]
Recovery	<ul style="list-style-type: none"> - Downstream processing losses are 16.5% - Electricity use of the rotary vacuum filter is 0.03 MJ, for the ultrafilter is 1.6 MJ, and for the reversed osmosis is 6 MJ - All pump efficiencies are 80% 	
Formulation	<ul style="list-style-type: none"> - 30% (w/w) is needed to stabilize the enzymes 	[33]
Biomass treatment	<ul style="list-style-type: none"> - Biomass and waste water receive a heat treatment at 394.15 K. Afterwards they are cooled, cooling water leaves at 368.15 K - Waste biomass and waste water are separated by a centrifuge till a 30% dry matter substance is obtained. The centrifuge uses 0.5 MJ/m³ 	[34] [35]
Assumptions brewing process		
Milling	<ul style="list-style-type: none"> - Milling malt and barley consumes 6.5 kWh/ton and 10.45 kWh/ton respectively 	[31]
Mashing	<ul style="list-style-type: none"> - Enzymes from malt and the exogenous enzymes are able to break down all starch in the brew (2 g/kg barley) - Conventional brewing uses 2.5 m³ water/ton grist and barley brewing uses 2.2 m³ water/ton grist. - All starch is hydrolysed into fermentable sugars 	[21] [31] [31]
Lautering	<ul style="list-style-type: none"> - 0.64 m³ sparging water/ton mash is used (345.15 K) - 14% of the wet weight ends up in the spent grains 	[31]
Wort boiling	<ul style="list-style-type: none"> - 4% water is evaporated during wort boiling 	
Coarse break & whirlpool	<ul style="list-style-type: none"> - 7 g/L is removed (80% water, 74% (dry matter) carbohydrates, 12% (dry matter) proteins and 13% (dry matter) fats) - Cooling water heats up to 366.15 K. Additional cooling to 280.15 K by ammonia. 	
Fermentation & maturation	<ul style="list-style-type: none"> - Temperature during fermentation is 280.15 K, cooled by ammonia - Only ethanol is formed, no higher alcohols - 2% of the fermentable sugars are used for yeast anabolism. 	
Filtration	<ul style="list-style-type: none"> - 2.25% w/w (wet weight) is removed as yeast after fermentation 	[29]
Pasteurisation	<ul style="list-style-type: none"> - All yeast is removed - Water is added to bring the beer to a 5%w/w alcohol - No evaporation of water or alcohol occurs 	

Table 3

Standard Molecular mass, chemical exergy and heat capacity of the used components.

Material	Molecular mass [kg/mol]	Standard chemical exergy [J/Kg] ^a	Heat capacities [J/kgK]
Water	0.01802	4.994E+04	4190
Steam	0.01802	5.272E+05	1840
Air	0.02896	-1.290E+03	1010
Carbohydrates (other)	227000 (of starch)	1.764E+07	1420
Carbohydrates (glucose)	0.1802	1.626E+07	1420
Proteins	3000 (of gluten)	2.261E+07	1550
Fat	0.2564 (of palmitic acid)	4.309E+07	1680
Ashes	0.06005 (of K ₂ CO ₃)	3.164E+04	837
Ethanol	0.04607	2.952E+07	2390
CO ₂	0.04401	4.516E+05	780
Glycerol	0.09202	1.850E+07	1629
O ₂	0.03200	1.241E+05	919
N ₂	0.02801	2.463E+04	1040
Ammonia	0.01703	1.980E+07	4520

^a Calculated from Ref. [27].

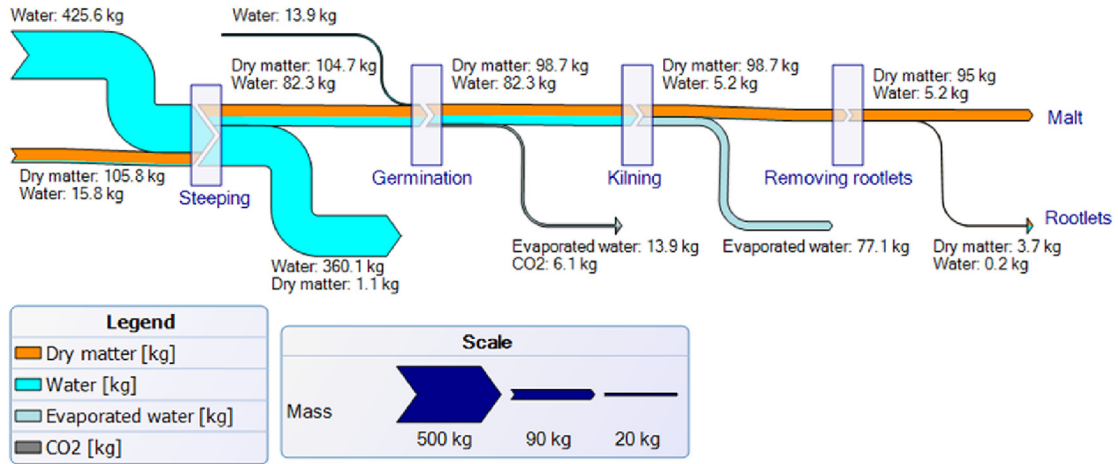


Fig. 2. Sankey diagram showing the mass of the streams of the conventional malting process for the production of 100 kg malt. The diagram excludes air (germination uses 3111 kg dry air, kilning uses 9535 kg dry air and cooling the kilned barley uses 288 kg dry air).

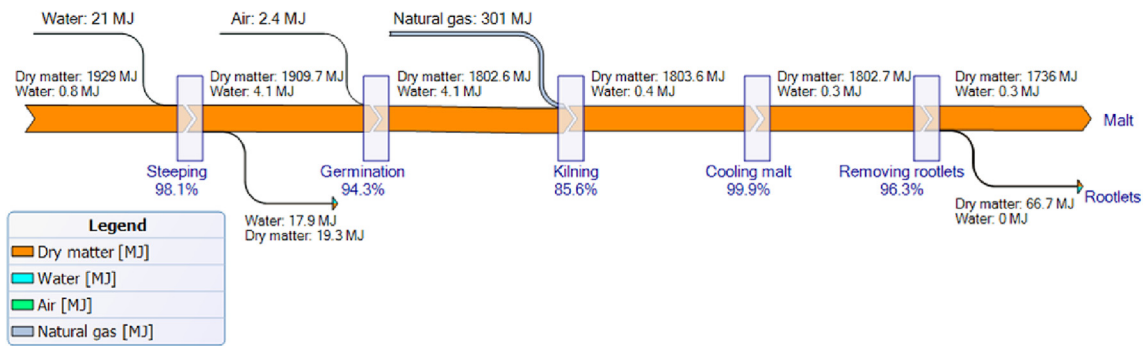


Fig. 3. Grassmann (exergy flow) diagram of the conventional malting process for the production of 100 kg malt.

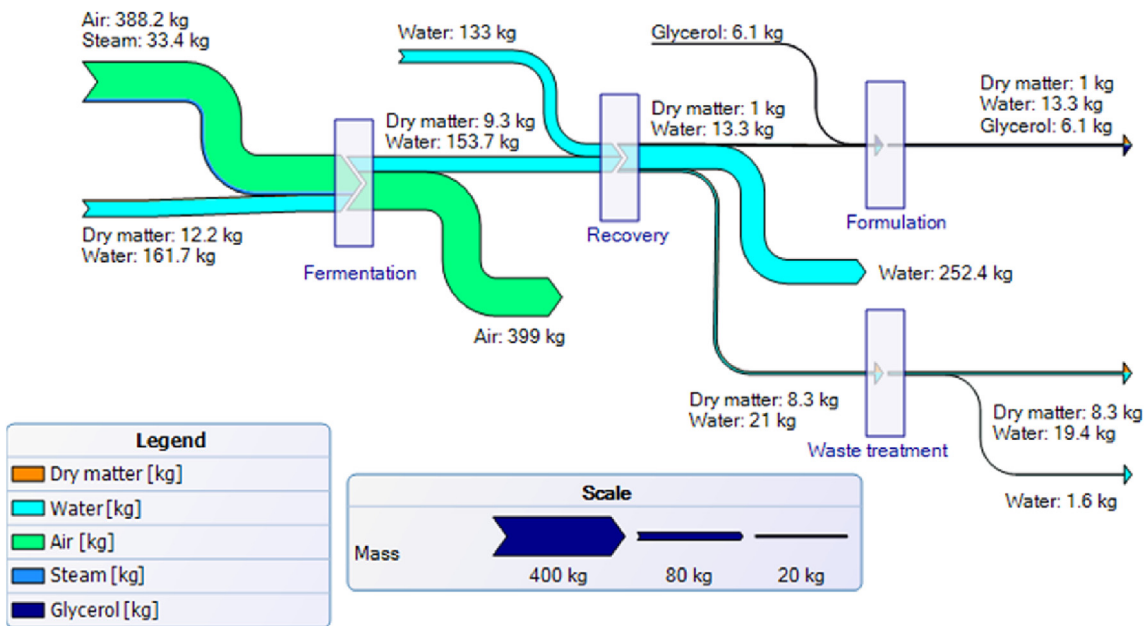


Fig. 4. Sankey diagram showing the mass of the streams of the enzyme production process for the production of 1 kg of enzyme. Diagram is excluding cooling water (3974 kg and 133 kg of cooling water in the fermentation and in the waste treatment, respectively).

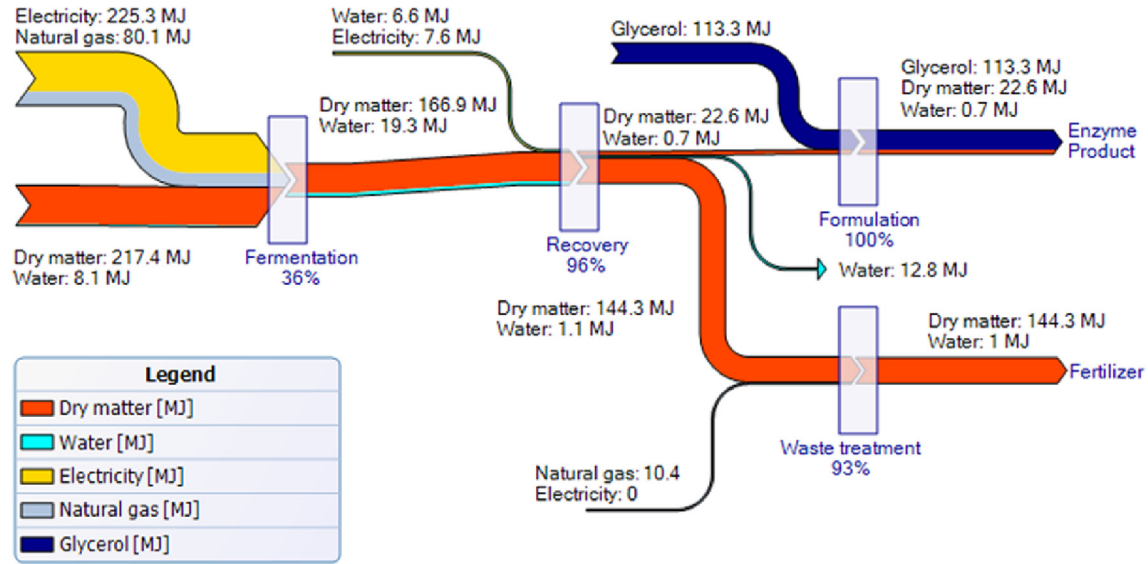


Fig. 5. Grassmann diagram of the enzyme production process for the production of 1 kg of enzyme. The standard chemical exergy of all heating and cooling agents are not illustrated.

Fertilizers are usually meant to enrich the soil in certain elements, for example nitrogen. However, in this particular side stream the amount nitrogen is reduced compared to the medium, and, though the amount is still sufficient to be used as a fertilizer, one could argue that this process is an inefficient way to produce fertilizer. In fact, the starting material would be a more efficient fertilizer. Second, fertilizer in general can be produced in much more efficient ways than in this process. Therefore, we decided to attribute all exergy losses to the production of the enzyme formulation itself and not to the fertilizer side stream.

Fig. 6 shows the amount of wasted and destroyed exergy per process step for both the conventional malting and the enzyme-assisted process. The exergy losses in the enzyme-assisted process are smaller than the exergy losses of the malting process when the amounts of enzymes or malt necessary for the production of 100 kg of beer are compared. The main reason is related to the small required dosing of only 33 g enzyme mix, which contains only 1.6 g of dry enzyme, per 100 kg of beer. Even if we assign all resources used to the enzymes, which accumulates to 676 MJ per kg enzyme, the small dosage of enzyme mix leads to a low cumulative exergy

consumption. The exergy losses for mashing, brewing and fermentation are similar in both processes. The mashing process contributes most to the wasted exergy while the fermentation process (together with malting in the conventional process) to the destroyed exergy. The wasted exergy of the mashing process is due to the material (i.e. chemical exergy) loss at the filtration process. The destroyed exergy in mashing is mainly caused by the heating of the mash. The exergy destruction in fermentation is due to losses caused by the use of part of the material as nutrient in the yeast metabolism. Typically, 2% of the sugars are used for the yeast metabolism, which explains the considerable loss in chemical exergy.

Fig. 7 depicts the percentage of wasted, destroyed and used exergy per process. Circumventing the malting step does not only reduce the total exergy input of the process but also prevents about 60 MJ/100 kg beer of exergy destruction. The reduced exergy input is partly due to the reduced water and energy use, and partly due to the lower amount of raw material needed. The latter is related to the fact that some starch is used during malting, and, therefore, more barley is needed to produce the same amount of beer.

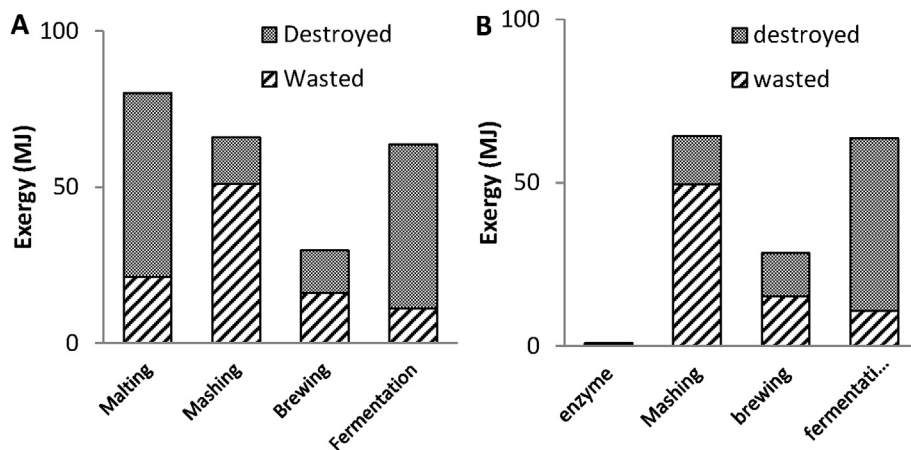


Fig. 6. Wasted and destroyed exergy in the different process stages of the industrial brewing process for producing 100 kg beer when: (A) conventional malting process is used, and (B) when enzymes are used.

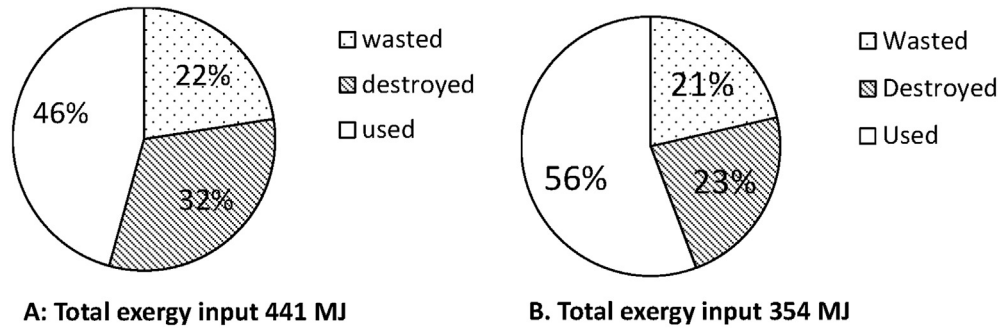


Fig. 7. Total exergy used, destroyed and wasted for the production of 100 kg of beer by using the: (A) conventional malting process, or the (B) enzyme-assisted process.

The exergy efficiencies of the complete processes are 45.7% for the conventional brewing process and 55.6% for the enzyme assisted process. Besides this, the total exergy input of the enzyme assisted process is also lower, implying that the use of enzymes instead of malting means a considerable improvement in exergetic sustainability of the process. If the fertilizer would be taken into account as useful output of the process, the exergetic efficiency would increase from 55.6% to 55.7%, which is a negligible increase, and this decision therefore does not affect the outcome of the analysis when the whole process is taken into account.

Fig. 8 shows the raw material use, water use, natural gas and electricity consumption, and exergy input for the production of 100 kg beer. The raw material use, water use and natural gas consumption were reduced by 14%, 7% and 78%, respectively. The air use was reduced by almost 2000 kg. The electricity input is the only parameter that increased, but only by 2.6%. These factors together resulted in a total decrease of 24% in total exergy input. Consequently, the use of raw barley brewed with the addition of exogenous enzymes is exergetically more efficient compared to the conventional brewing process.

In the enzyme assisted process, only 1 MJ of the total 354 MJ of exergy necessary to produce 100 kg of beer is due to the enzyme production process. This is only 0.31% of the total exergy input of the process, and therefore the CExC of enzymes does not significantly contribute to the total CExC of beer. The amount of enzyme needed to make the enzyme assisted process equally efficient as the malting process would be more than 80 times as much as what is used at the moment. This would be a very unrealistic value. As these amounts of enzymes will never be used in enzyme assisted processes, it can be concluded that enzymes are useful to make processes more resource efficient.

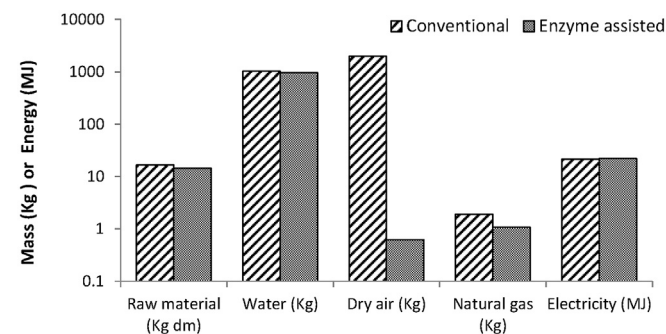


Fig. 8. Amount of raw materials, water, dry air, natural gas and electricity used in the production of 100 Kg beer when using the: (A) conventional malting process, or the (B) enzyme-assisted process.

4. Conclusions

This paper compares two processes for making beer at industrial scale. One process is the conventional process, while the other process is an enzyme-assisted brewing in which the malting step is omitted. The analysis showed that the enzyme-assistant process has a reduced impact on the environment. Circumventing the malting step reduces the use of water by 7%, of raw materials by 14%, and of natural gas by 78%. The CExC of specific additives (for example enzymes), can be considerably higher than just their standard chemical exergy. In case of enzymes, we found that the CExC of enzymes is about 676 MJ/kg dry enzyme, which is 30 times the standard chemical exergy value.

Whether the CExC of an additive considerably affects the outcome of the thermodynamic analysis of a process depends both on the amount of the ingredient required, and on the way this ingredient was produced. A large requirement of an ingredient of high CExC can have a large impact on the exergetic efficiency of the analysed process.

Funding

Institute for Sustainable Process Technology (ISPT), Amersfoort, The Netherlands.

Acknowledgements

This research took place within the ISPT framework (Institute for Sustainable Process Technology). We would like to thank ISPT and Heineken for their financial support and fruitful discussions.

References

- [1] Olajire AA. The brewing industry and environmental challenges. *Journal of Cleaner Production*. In press (available online March 2012).
- [2] Cimini A, Moresi M. Carbon footprint of a pale lager packed in different formats: assessment and sensitivity analysis based on transparent data. *Journal of Cleaner Production*.
- [3] Cordella M, Tugnoli A, Spadoni G, Santarelli F, Zangrando T. LCA of an Italian lager beer. *Int J Life Cycle Assess* 2008;13(2):133–9.
- [4] Hospido A, Moreira MT, Feijoo G. Environmental analysis of beer production. *Int J Agric Resour Gov Ecol* 2005;4(2):152–62.
- [5] Simate GS, Hill AE. 20-Water treatment and reuse in breweries. *Brewing Microbiology*. Oxford: Woodhead Publishing; 2015. p. 425–56.
- [6] Pérez-Bibbins B, Torrado-Agrasar A, Salgado JM, Oliveira RPdS, Domínguez JM. Potential of lees from wine, beer and cider manufacturing as a source of economic nutrients: an overview. *Waste Manag* 2015;40:72–81.
- [7] Köroğlu EO, Özkaya B, Denктаş C, Çakmakci M. Electricity generating capacity and performance deterioration of a microbial fuel cell fed with beer brewery wastewater. *J Biosci Bioeng* 2014;118(6):672–8.
- [8] Aliyu S, Bala M. Brewer's spent grain: a review of its potentials and applications. *Afr J Biotechnol* 2013;10(3):324–31.
- [9] van Donkelaar LHG, Noordman TR, Boom RM, van der Goot A-J. Pearling barley to alter the composition of the raw material before brewing. *J Food Eng* 2015;150(0):44–9.

- [10] Dincer I, Ratlamwala TAH. Importance of exergy for analysis, improvement, design, and assessment. *WENE* 2013;2(3):335–49.
- [11] Szargut J. Second law analysis of energy devices and processes International progress in second law analysis. *Energy* 1980;5(8):709–18.
- [12] Apaiah RK, Linnemann AR, van der Kooij HJ. Exergy analysis: a tool to study the sustainability of food supply chains. *Food Res Int* 2006;39(1):1–11.
- [13] Rosen MA, Dincer I, Kanoglu M. Role of exergy in increasing efficiency and sustainability and reducing environmental impact. *Energy policy* 2008;36(1):128–37.
- [14] Özilgen M, Sorgüven E. Energy and exergy utilization, and carbon dioxide emission in vegetable oil production. *Energy* 2011;36(10):5954–67.
- [15] Berghout JAM, Pelgrom PJM, Schutyser MAI, Boom RM, van der Goot AJ. Sustainability assessment of oilseed fractionation processes: a case study on lupin seeds. *J Food Eng* 2015;150:117–24.
- [16] Aghbashlo M, Mobli H, Rafiee S, Madadlou A. Energy and exergy analyses of the spray drying process of fish oil microencapsulation. *Biosyst Eng* 2012;111(2):229–41.
- [17] Quijera JA, Labidi J. Pinch and exergy based thermosolar integration in a dairy process. *Appl Therm Eng* 2013;50(1):464–74.
- [18] Jankowiak L, Jonkman J, Rossier-Miranda F, Goot AJvd, Boom RM. Exergy driven process synthesis for isoflavone recovery from okara. *Energy* 2014;74:471–83.
- [19] Draganovic V, Jørgensen SE, Boom R, Jonkers J, Riesen G, van der Goot AJ. Sustainability assessment of salmonid feed using energy, classical exergy and eco-exergy analysis. *Ecol Indic* 2013;34:277–89.
- [20] Zisopoulos FK, Rossier-Miranda FJ, Van Der Goot AJ, Boom RM. The use of exergetic indicators in the food industry—a review. *Crit Rev Food Sci Nutr* 2015 (just-accepted):00–.
- [21] Steiner E, Auer A, Becker T, Gastl M. Comparison of beer quality attributes between beers brewed with 100% barley malt and 100% barley raw material. *J Sci Food Agric* 2012;92(4):803–13.
- [22] Evans DE, Redd K, Harraysmow SE, Elvig N, Metz N, Koutoulis A. The influence of malt quality on malt brewing and barley quality on barley brewing with Ondea Pro, compared by small-scale analysis. *J Am Soc Brew Chem* 2014;72(3):192–207.
- [23] Goode D, Wijngaard H, Arendt E. Mashing with unmalted barley - impact of malted barley and commercial enzyme (*Bacillus* spp.) additions. *Tech Q Master Brew Assoc Am* 2005;42(3):184–98.
- [24] Kunz T, Müller C, Mato-Gonzales D, Methner FJ. The influence of unmalted barley on the oxidative stability of wort and beer. *J Inst Brew* 2012;118(1):32–9.
- [25] Kribs JD, Spolek GA. Drying energy conservation for deep-bed barley-malt kilns. *J Agric Eng Res* 1997;68(4):367–73.
- [26] Nielsen P, Oxenbøll K, Wenzel H. Cradle-to-gate environmental assessment of enzyme products produced industrially in Denmark by novozymes A/S. *Int J Life Cycle Assess* 2007;12(6):432–8.
- [27] Szargut J. Chemical exergies of the elements. *Appl Energy* 1989;32(4):269–86.
- [28] Jones A, Lamsa M, Frandsen TP, Spendler T, Harris P, Sloma A, et al. Directed evolution of a maltogenic α -amylase from *Bacillus* sp. TS-25. *J Biotechnol* 2008;134(3):325–33.
- [29] Kunze W. *Technology brewing & malting*. fourth ed. Berlin: VLB Berlin; 2010.
- [30] Lewis MJ, Young TW. *Brewing*. Chapman & Hall; 1995.
- [31] Kløverpris JH, Elvig N, Nielsen PH, Nielsen AM. In: Comparative life cycle assessment of malt-based beer and 100% barley beer. *Novozymes*; 2009.
- [32] Alber W, Hahn M, Klade M, Seebacher U, Spok A, Wallner K, et al. In: *Collection of information on enzymes*. Commission E; 2002.
- [33] Gill N, Appleton M, Baganz F, Lye G. Quantification of power consumption and oxygen transfer characteristics of a stirred miniature bioreactor for predictive fermentation scale-up. *Biotechnol Bioeng* 2008;100(6):1144–55.
- [34] Albaek MO, Gernaey KV, Hansen MS, Stocks SM. Modeling enzyme production with *Aspergillus oryzae* in pilot scale vessels with different agitation, aeration, and agitator types. *Biotechnol Bioeng* 2011;108(8):1828–40.
- [35] Bradbury SL, Jakoby WB. Glycerol as an enzyme-stabilizing agent: effects on aldehyde dehydrogenase. *Proc Natl Acad Sci* 1972;69(9):2373–6.
- [36] Zisopoulos FK, Moejes SN, Rossier-Miranda FJ, van der Goot AJ, Boom RM. Exergetic comparison of food waste valorization in industrial bread production. *Energy* 2015;82:640–9.
- [37] Szargut J, Morris DR, Steward FR. *Exergy analysis of thermal, chemical, and metallurgical processes*. New York: Hemisphere; 1988.