EXERGY FLOWS IN INDUSTRIAL PROCESSES

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Abstract

The concept of exergy is defined and applied to industrial processes. The study discusses the meaning of the choice of definition of efficiency, system limitations and problem definition. The exergy flows for a pulp and paper mill and a steel plant are presented. The study establishes the energy flows in processes and draws up the exergy losses. For the purpose of comparison, the Swedish space heating system is described using the exergy concept. The energy and exergy prices of several common energy forms are compared.

The aim of this report is to show the simplicity and the value of using the concept of exergy when analyzing industrial processes and to develop conventions and standards within the field. The large losses which are revealed in an exergy treatment of a process should be seen as a challenge to achieve technical improvements, not as an insurmountable obstacle.

The author welcomes opinions, comments and critical reviews of this study.

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1. SUMMARY

The report begins by defining concepts that are important for exergy studies. Exergy is defined as the work that can be extracted when a system is brought into equilibrium with its surroundings without incurring any losses (Wall 1977). The efficiency of a process is here defined as the used exergy outflow divided by the used exergy inflow.

Our ability to find new solutions is often limited by the existing technology. We often overestimate current technology in relation to past technology and to future alternatives. Thus, today’s most sophisticated computers are mere “steam engines” when compared to the simplest biological cell or to future computers as is also illustrated by the rapid developments in the computer field. This paper emphasizes therefore the importance of defining the problem in scientific terms, that is, unhindered by the limitations of current technology. Such a description must, of course, be based on clearly defined scientific concepts. Unfortunately, this is not always the case with the result that our picture of reality is false and may consequently constitute an obstacle to important technological advances.

This study presents in more detail the energy and exergy flows of two typical Swedish industries, a pulp and paper mill and a steel plant. These are also described in relation to Sweden’s space heating system. The pulp and paper industry described is SCA-Nordliner in Munksund which produces unbleached kraft liner, see Fig. 5.1. After the wood is cleaned, debarked and chipped, the wood chips are processed in a continuous digester to a sulphate pulp. The separated bark is combusted together with fuel oil to produce steam and electricity both of which are used in the process. The chemicals and the stripping (or draw-off) liquor leave the digester after processing. A major part of the chemicals is recovered in the flash and heat exchangers, evaporators, soda recovery unit and lime sludge reburning kiln, while the liquor is used to produce steam. The washed sulphate pulp is then transported to the paper mill where it is formed, dewatered, pressed, dried, reeled and cut for delivery. Approximately 36% of the energy losses are incurred in the soda recovery unit, approx. 17% in the steam production unit (or steam production unit), and approx. 34% in the paper mill. In terms of exergy losses, approx. 40% are incurred in the soda recovery unit, approx. 31% in the steam production unit and approx. 16% in the paper mill, see Table 5.1 and Fig. 5.2. The sum of the energy and the sum of the exergy losses in these three sub processes is the same, but the relative proportions in the two treatments vary considerably. Furthermore, seen from an energy point of view, the unutilized outflows (or waste flows) amount to 57% of the total losses as compared to an exergy loss of only 7%. It can be seen that these flows constitute a considerably smaller resource than an energy treatment leads us to believe, and it may thus be concluded that an energy treatment paints an incorrect picture of the process.

The steel plant is represented by Halmstads Järnverk which produces reinforcing steel from scrap iron, see Fig. 6.1. The scrap iron is melted in two electric steel furnaces and

then undergoes continuous casting. The steel is subsequently cut into blanks which are then reheated in a pusher type furnace and then rolled to circular crossections with diameters from 6 to 32 mm. The major part of the energy losses is incurred in the electric steel furnaces and during continuous casting, and amounts to approx. 44% of the total losses. The picture of the losses is more or less the same when we look at the exergy losses, see Table 6.1 and Fig. 6.2. Nearly half of the exergy losses are incurred in these two sub processes. The difference between the energy and the exergy treatments increases when we look at the unutilized flows in the process such as exhaust gases and heat. These account for approx. 65% of the energy losses but only for about 28% of the exergy losses. What appears as a substantial unutilized resource flow in terms of energy is thus shown to be considerably less in terms of exergy, which is mainly due to the temperature of the flows. Thus, only a minor improvement in efficiency can be achieved by utilizing the existing unutilized flows. It is only by introducing new more efficient processes that major improvements can be achieved.

As a comparison to the industrial processes, the study also describes the Swedish space heating system. This comparison reveals many interesting differences. The Swedish space heating system represents the largest single exergy saving potential in the country. The efficiency of conversion to heat is estimated to be about 5% for Sweden as a whole. Two observations can be made - one, that new technology offers enormous potential for improving Sweden’s space heating system, and two, that current-day systems are highly inefficient. Modern nuclear energy technology, which utilizes only a small fraction of the exergy content of nuclear fuel yields an extremely low efficiency in space heating.

Finally, the study provides a short description of the price of several of the most common energy forms in relation to energy and exergy content. This is relevant since the design of the energy system mostly depends on the price of different energy forms. The approximate energy price of electricity in SEK/GJ is about 70, gasoline about 110, fuel oil about 50, wood about 20, and district heat about 60. The high price of gasoline can be justified by its special area of use, the low price of wood can be explained by the fact that efficient energy production from wood is expensive. In terms of exergy, we obtain instead the following prices (SEK/GJ): electricity about 70, gasoline about 120, fuel oil about 50, wood about 20, and district heat about 340. The very high exergy price of district heat is difficult to justify but can be explained by today’s rather inefficient heat production technology. This means that it will hardly be possible to maintain the price of district heat as heat pump technology develops further. In the future, when heat pumps will have a coefficient of performance (COP) of about 5, the relative price of district heat will be about 5 times too high.

The method presented in this report is also valuable for long-term planning of, for example, research efforts on more efficient allocation of resources since it reveals the real losses.

2. INTRODUCTION

The concept of exergy is coming into increased international use. Many books published over the recent years have been based on the concept of exergy (Ahern 1980, Baehr 1978, Chapman 1983, Edgerton 1982, Moran 1982), many conference reports (Reis 1985, Gaggioli 1980, 1983, Wolfe 1975, Penner 1980) as well as a good many articles within a number of sub fields (Eriksson 1984, Marín 1986, Siemons 1986, Stecco 1986). Nonetheless, the concept of exergy is uncommon in describing industrial processes. This is unfortunate, particularly as I am absolutely convinced that the concept of exergy will become standard for all process analysis in the near future. This concept is both readily understood and easy to apply. The present report is based on an earlier work (Wall 1983) and has been adapted for a wider audience. Hopefully it will contribute towards a deeper understanding of the concept of exergy and increase the area of its use. The report is primarily intended for persons directly connected with energy and materials processing within business and industry. However, it is written in such a way that persons with a different background can without difficulty partake in the study and its conclusions. Detailed information such as tables and computer programs are presented in the appendixes. The objective is not to describe the calculation methods in exhaustive detail, but to more concisely point out the value of this method and provide new insights and conclusions.

The main objective is to show the applicability of the exergy for studies of industrial processes. The concept of exergy provides an estimate of the minimum theoretical resource requirement (requirement for energy and material) of a process. This in turn provides information on the maximum savings that can be achieved by making use of new technology and new processes. New technology and new processes do not come about by themselves. By giving a deeper insight into processes, the exergy concept provides a better foundation for improvement and for calculating expected savings. As a complement to the present materials and energy balances, exergy calculations can provide increased and deeper insight into the process, as well as new unforeseen ideas for improvements.

Another important goal is to establish standards as soon as possible in order to facilitate application in industry and in other planning processes such as energy planning.

3. DEFINING THE CONCEPT

Energy is often defined as work or the ability to perform work. This is wrong. Energy should instead be defined as motion or the ability to produce motion. This is certainly a less specific but a more correct definition. Energy can be defined as that which is indestructible or that which is always conserved during every closed process. Energy is thus most often an all too hazy concept.

S. Carnot described the relationship between work and heat (energy) as early as 1824:

$$W = Q\,(T - T_o)/T \tag{1}$$

where W is work that can be extracted when heat Q flows from a heat reservoir with an absolute temperature T to a reservoir with an absolute temperature T_o. (Note that the reservoirs' temperatures are not affected by the heat flow between them.)

During 1873-1878 J. W. Gibbs published three works from which it could be read that the work that can be extracted from a body in its surroundings is:

$$W = U + p_oV - T_oS - \sum \mu_{io} n_i \tag{2}$$

where U, V, S, and n_i are the body's internal energy, volume, entropy and the number of moles of substance "i", and p_o, T_o and μ_{io} are the ambient pressure, temperature, and the chemical potential of substance "i", respectively. This fundamental expression is the basis for all subsequent work. The only thing that needs to be added is that for a flow we obtain the expression:

$$W = H - T_oS - \sum \mu_{io} n_i \tag{3}$$

where H=U+pV is enthalpy and where chemical potential can be generalized to include other potentials such as electrical, magnetic and mechanical potential.

The term *exergy* (Ger. *exergie*) was proposed by Z. Rant as late as 1953 in order to describe work in this context. A complete definition was given by H. D. Baehr in 1965:

Die Exergie ist der unbeschränkt, d.h. in jede andere Energieform umwandelbare Teil der Energie. (Exergy is the totally convertible part of the energy, i.e. that part which may be converted into any other energy form.)

Thus, exergy is work extracted when a system is brought into equilibrium without incurring any losses.

Unfortunately, the concept of exergy has been attributed with many unnecessary names. Technische Arbeitsfähigkeit (technical ability to perform work), available work, availability, available energy and essergy - the essence of energy, are all names for generally the same thing, namely, exergy. In everyday language it is even often the case that one means exergy when one speaks about energy, for example, energy consumption.

The concepts of energy and exergy are related to the first two laws of thermodynamics: **1st law**: *Energy is constant in a closed system* (compare with: that which is constant in a closed system is called energy which is a more accurate/correct formulation). **2nd law**: *Heat can only move spontaneously from a higher to a lower temperature*, which yields work determined by exergy for heat in relation to transition. To analyze the process in terms of the 2nd law of thermodynamics is thus analogous to using the concept of exergy. (From the point of view of electrical science, we can treat energy as a kind of standard potential and exergy as voltage in relation to our chosen surroundings.)

The exergy of a system may also be written as (Wall 1977):

$$E = S(T - T_o) - V(p - p_o) + \sum n_i(\mu_i - \mu_{io}) \tag{4}$$

where we clearly see that exergy approaches zero as the system approaches equilibrium with the environment. We also see that exergy here is expressed as the sum of terms for differences in temperature, pressure and chemical potential. As I mentioned above, the effects of electricity, magnetism, gravity, radiation, etc. can also be added to this expression.

Analogously, the exergy of a flow can be written as:

$$E = H - H_o - T_o(S - S_o) - \sum \mu_{io}(n_i - n_{io}) \tag{5}$$

with the result that the exergy of a steam flow, for example, can simply be calculated from conventional steam tables. A computer program in BASIC has been developed in order to calculate steam data with table accuracy on a microcomputer (PC), see Appendix 3. This has previously only been possible on large computers (Keenan et al. 1978, Reynolds 1979).

For mixtures of substances, the calculation of exergy content is somewhat more complicated. The enthalpy can be calculated as the sum of the enthalphies of its substances. The entropy of a mixture, on the other hand, is determined by its nature. An ideal mixture is one where the elements are completely intermixed, i.e. two mixed gases or a drop of ink dissolved in water. The entropy of such mixtures is:

$$S = \sum x_i s_i - R\sum x_i \ln x_i \tag{6}$$

where x_i is the molar ratio of substance i, and R the gas constant.

There is no general theory or unequivocal concept for non-ideal mixtures. (This may be noted as serious in terms of the significance of these mixtures). Examples of non- ideal mixtures are alloys, suspensions and emulsions. It has been assumed here that the entropy of such mixtures is the sum of the entropies of the mixed substances, i.e., the last term which gives the entropy of the actual mixing process in Eq. (6) is excluded.

Data on thermal capacities is only available for pure elements and for certain chemical compounds such as oxides (Weast 1983 and U S Atomic Energy Report). That is why the thermal capacity of a mixture has been assumed to be the sum of the values of the substances in relation to their proportion. However, the result is that the mixtures where new phases appear are attributed incorrect values for thermal capacity. However, the size of this error is considered negligible in relation to errors in other data such as quantities and temperatures. The method of calculation is shown in Appendix 4, which is the BASIC program for calculating the thermal and chemical energy and exergy of an arbitrary mixture of certain substances under constant pressure.

Efficiency is a very valuable concept for describing the workings of a process. Usually we use the value 1 or 100% as the maximum efficiency. Unfortunately, this does not always apply when using the concept of energy. A maximum efficiency of hundreds of percent is not unusual, see Chapter 7. When calculating efficiency, it is also very important to clearly define system boundaries. Efficiency is here defined as useful energy/exergy output divided by the energy/exergy utilized in the process, that is the incoming quantity of energy/exergy minus the outgoing quantity that is not used. As a result, the efficiency of processes with large waste flows may be high. Efficiency may also be defined as the utilized outflow divided by the direct inflow indispensable for the process or as the minimum theoretical exergy requirement divided by the actual exergy requirement. One problem that applies to both of the former definitions is that processes where the energy/exergy flow passes through the process more or less unaffected yield an ostensibly high efficiency, that is, nearly 100%, for example, this may apply to a high temperature heat flow passing through a process where the temperature is raised only one or two degrees with relatively large losses. For the latter definition, it is true that an exact calculation of the minimum theoretical exergy requirement is difficult to make. Thus, each choice of definition entails both advantages and disadvantages. The efficiencies of certain processes in the study are also calculated, these are given in Appendixes 1 and 2. However, efficiency is an altogether overly simple measure for a good description of a process and can never replace a more detailed analysis.

The study does not include indirect “resource costs”, such as the energy and materials necessary for manufacturing fixed capital, i. e. machines. The term energy/exergy *analysis* should be reserved for such studies (Wall 1977).

4. DEFINING THE PROBLEM

The following two examples illustrate the importance of a clear problem definition (Andersson 1981).

(1) When Gustav III (1746-1792) of Sweden wished to send a message, it was natural for him to think of a messenger on horseback. Taking this train of thought a little further, a research program for improving communication methods would consequently have entailed a commitment towards improving horse-breeding methods. An energy analysis of the function of sending a message from Stockholm to Göteborg, for instance, would have resulted in a study of horse eating habits. However, with time, it was realized that neither horses nor couriers were necessary in order to transfer a message. Neither were letters in themselves, that is, paper and ink, necessary. Experiments with optical telegraph chains came under way and, with time, messages could be sent by cable, and today even via satellite.

(2) Today, when we set about to estimate the energy requirement for cutting a log of lumber into boards, we start out by assuming that the lumber will be sawn. When the price of fuel goes up, we begin by examining whether the process can be improved by selecting a more efficient motor to drive the saw-blade. We conclude that electric motors are usually 90% efficient and that it is thus not possible to achieve more than a 10% improvement. But in scientific terms, cutting results in two surfaces of a section which are separated so that the forces of attraction are negligible, i.e. a distance of several atom diameters. If one considers that wood has an ultimate strength of 10^4 N/cm^2 and that the distance required to separate the surfaces is $3 \cdot 10^{-9}$ m (10 times the diameter of a water molecule), it takes less than 0.3 J to cut a log 5 m long and 20 cm in diameter. Thus 1 kWh should suffice to cut 10 millions logs. However, a saw not only creates two new surfaces, but also the surface around each sawdust. Consequently, in the best of cases, a saw with a 1 kW motor can cut 300 logs of lumber per hour, i.e. 30 logs per kWh. Hence, it is not true that we can reduce the energy requirement by a maximum of 10%. We can reduce the requirement by more than 10^5 if we find better methods than cutting.

The seemingly high efficiency of today’s computers fades in the light of comparison with the simplest biological cell. Reproducing a DNA molecule in a cell is at least 10^9 more efficient (Wall 1977). In this perspective, biotechnology appears to have enormous technical potential for development well worth a commitment.

These examples are not selected to diminish existing technology, but to put it in a scientific perspective. This is the only way we can perceive the enormous potential of existing technology. We must learn to view the shortcomings of current-day technology as a challenge for improvement, not as an insurmountable obstacle.

The following description is a proposal for an adequate study and description of technological processes (Edgerton 1982, Wall 1985):

- Briefly describe the system to be studied
- Define the system, system boundaries, components, and various subsystems, etc. (A flow diagram is often the best way to define the system, sometimes it is also necessary to draw a schematic picture of the system.)
- Define those physical properties of the immediate surroundings that are important for the system, such as temperature and pressure. These are the reference conditions to which all resource flows are related.
- Give the conditions and approximations as well as sources for an analytical description of the process.
- Calculate the material balance used in the process by giving the necessary thermodynamic qualities of each flow.
- Calculate the energy balance
- If possible, describe the thermodynamic relationships of each component
- Calculate the exergy of all of the flows in the process and the exergy losses of each component. If possible, state the reason for the exergy losses.
- Suggest possible improvements

This method of working is, of course, obvious for the most part and standard practice. The most important difference, however, is the taking into account of the immediate surroundings and its effects on the system. That in itself allows us to introduce and apply the exergy concept and thus calculate the real losses in the process. As an example of the application of this method, I have selected a pulp and paper mill, a steel plant, and the Swedish space heating system.

5. A PULP AND PAPER MILL

The following two chapters describe a number of subprocesses in the steel and pulp and paper industry. In those cases where the descriptions are based on earlier energy studies which at times lacked sufficient data for making exergy calculations, estimates have been made. Certain data have been changed when they were shown to be obviously wrong during the exergy calculations. In order to simplify the description, the minor flows were neglected. Efficiency, defined as utilized outflow divided by utilized flows, is also given. Other efficiencies are also given for certain processes such as heating of steel.

The data used in this chapter is based on an energy study by Jan Fors and Börje Nord in 1980 of a pulp and paper industry - SCA-Nordliner i Munksund and contacts with chief of operations at the mill, Bo Häger, as well as on litterature (Ejderby 1976, Libby 1962, MacDonald 1969, Sittig 1977, Marín 1986). The mill annually produces 265 000 tonnes of unbleached kraft liner from 210 000 tonnes of unbleached sulphate pulp and 55 000 tonnes of recycled waste paper which is used mostly as raw material for corrugated fiberboard. The plant, which consists of the sulphate pulp factory and of the paper mill, is schematically illustrated in Fig. 5.1. The process may be briefly described as follows:

- The wood is separated from the bark. The bark is combusted in a steam production unit and the wood chipped.
- The chips are cooked with white liquor at high pressure in the continuous digester.
- The pulp and liquor are removed from the bottom of the digester by a blower mixer, to be screened, washed and refined.
- The pulp is then dried in the paper mill by dewatering, pressing and through evaporation.

The material flows of every subprocess given in tonne per tonne of produced paper (tonne/tp), and the energy and exergy flows in MJ/tp are presented in Appendix 1. Note that the paper mill supplies fiber via waste paper which accounts for the fact that the real production of pulp in a pulp factory is equivalent to a production of approx. 0.78 tonnes of paper. (In order to obtain values in tonne per tonne of pulp, this should be multiplied by a factor of 1.22.) The yield of the process, given as quantity of dry wood (fiber) in the paper, is 57%.

Table 5.1 gives the assumed chemical composition of the flows in the process. Figure 5.2 shows the exergy flows in the entire process. (It is interesting to compare this diagram to the energy flow (Fors and Nord 1980)). The most exergy-intensive processes are readily distinguishable. It is also interesting that large quantities of exergy in the form of liquor and black liquor (or concentrated waste liquor) circulate through the process. The circuit of the processing chemicals in the stripping liquor, mixed (or semi thickened) liquor, black liquor, green liquor and white liquor can also be readily discerned. A description of each subprocess is given below.

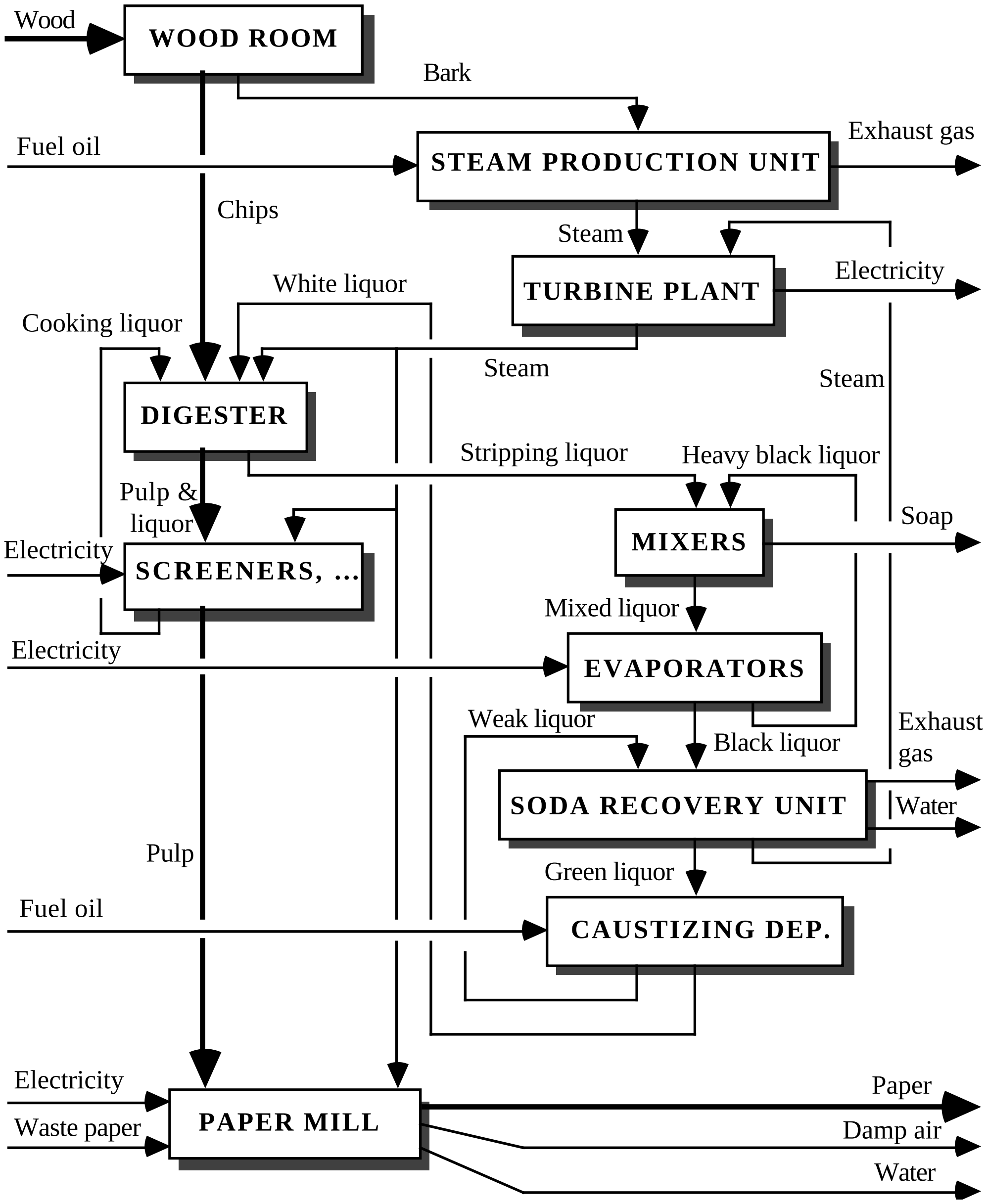

Fig. 5.1. A pulp and paper mill

Fig. 5.2. Exergy flow trough a pulp and paper mill

Table 5.1. Assumed chemical composition of substances in the pulp and paper mill

Substance	H	H_2O	C	O	Na_2CO_3	NaOH	Na_2S
Stripping liquor	0.6	85.8	4.7	3.9	0.9	2.5	1.6
Bark[a]	2.4	60.0	20.0	17.2			
Mixed liquor	0.9	76.2	7.4	6.4	1.7	4.5	2.8
Green liquor		80.8			14.0		5.2
Liquor	0.7	88.7	6.9	3.3	0.1	0.2	0.1
Pulp	0.8	87.1	6.3	5.8			
Pulp & liquor	1.4	78.0	12.4	7.6	0.1	0.3	0.2
Paper/kraft liner	5.8	7.6	45.0	41.6			
Waste paper	4.6	26.4	35.9	33.1			
Waste liquor	0.9	77.2	7.5	6.2	1.5	4.1	2.6
Weak liquor		95.9			3.0		1.1
Soap	4.7	27.6	46.9	20.9			
Black liquor	3.3	39.6	18.8	16.3	4.2	11.5	7.2
Wood/chips	3.1	50.0	25.0	21.9			
White liquor		83.2			3.1	8.4	5.3

[a]0.4% N

Wood room

The incoming wood is separated from ice and snow with hot water prior to debarking in the barking drum (bark quantity 0.44 tonnes/tp). The ice (0.70 tonnes/tp) is melted and heated with hot water to 30°C. The bark is pressed in order to reduce its water content from 65-70% to below 60% and thus upgrade its fuel value. The bark is then transported in a blowoff pipe to the steam production unit where it is combusted. The debarked logs are heated with hot water to 25°C and chipped (2.67 tonnes/tp). This increases the wood's energy value. The exergy of the wood, however, is reduced, since -16°C represents a contrast in temperature which disappears when the wood is assumed to be heated to 25°C, which is the given reference temperature. (This temperature agrees with the general standard (Weast 1983).) Electricity is used for debarking, chipping and dewatering of the bark in a bark press. A large quantity of effluent (6.13 tonnes/tp) builds up at a low temperature (30°C). The energy and exergy losses are, as we see, minor, see Appendix 1, which results in high efficiency values, 99.8% and 99.0%.

Continuous digester

The digester is continuous and of the KAMYR type. The wood chips and white liquor are continuously fed into the upper part of the digester while the pulp is removed from the lower part (of the digester) using liquor (pulp and liquor: 10.64 tonnes/tp). The processing chemicals, which are removed with the stripping liquor, are recovered by means of the white liquor. The chips are not fed directly into the digester. First, they pass through a steaming vessel which maintains a pressure of approx. 0.25 MPa. The chips are subsequently fed into a high pressure feeder with several rotating bins. This way, the chips can be fed from a bin to the top of the digester while another bin is being filled with chips and liquor. The digester is filled at all times and maintains a overpressure of 1 MPa. As we can see, the losses are once more minor and the efficiencies high.

Screening, washing and refining

The pulp is pulverized, refined and separated from the liquor. Knots and fiber bundles are broken up in the primary refiner. The cleansing liquid is brought in at the top in a continuous diffuser and pressed through the pulp. The liquor, which is heavier than water, is thus pushed out through the perforated bottom. Impurities larger than the pulp fibers are separated through screening. That pulp which passes through the screen is called accept and is used as the upper layer in the production of kraft liner. The pulp which does not pass through the screen is called reject pulp and is used for the bottom layer of the kraft liner. Both the accept and the reject pulp is subsequently washed in a washing filter consisting of rotating cylinders which are densely perforated and covered with a metal gauze. The remaining liquor is sucked out by the low pressure on the cylinder’s inner side. The pulp is rinsed with water above the water level of the tray in order to improve its washing effect. Finally, the pulp is refined once more prior to being pumped via storage tanks to the paper mill. Whenever large quantities of hot water with a low exergy content are used, the energy losses are higher than the exergy losses. Consequently, the exergy efficiency (99.1%) is higher than the energy efficiency (98.4%).

Mixers and heat exchangers

The liquor leaving the digester is thickened by being mixed with the black liquor to enable it to be processed in the evaporator. Mixing of the concentrated liquor prevents foaming in the evaporator and reduces the evaporator’s energy consumption. Mixing takes place in stages which, at the same time, yields valuable steam. Subsequent to the first inmixing, the concentrated waste liqour is brought into a mixing tank which maintains a pressure of 0.27 MPa. A part of the water content of the liquor is evaporated when the pressure is lowered. The steam released in this way is utilized in the digester’s steaming vessel. In the other mixing tank with a pressure of 0.14 MPa, the steam is flashed to a column where it is condensed and the built-up liquor vapor condensate is pumped to wash-water tanks.

The liquor is then exchanged with cold water which is heated to 55°C in order to be used in other processes. The waste liquor and the heavy black liquor are mixed while the soap is skimmed off from the readymade liquor surface as a by-product before the mixed liquor is pumped to the evaporation plant. The soap, which has been dissolved in the water, sharply reduces its solubility when the liquor is thickened, forms a coating on top of the liquor, and can be thus easily skimmed off. The soap is boiled to resin oil (liquid resin or tall oil) in a resin boiling plant and sold. Production amounts to 45 kg of resin oil per tonne of pulp.

We can note from Fig. 5.2 that the exergy content of the incoming cold water, at 24°C below the reference temperature, is 31 MJ/tp, i.e. higher than for the same quantity of outgoing hot water at 55°C, 21 MJ/tp, i.e. 30°C higher than the reference temperature.

Evaporator plant

The mixed liquor is evaporated to about 60% of dry content (black liquor) by being steamed in order to be more efficiently combusted later in the soda recovery unit. In order to keep steam consumption to a minimum, this process takes place in several steps at successively lower temperatures and pressures. The liquor is brought in through the bottom part of the unit in tubes which are heated with steam on the outside. The upper part of the evaporator has a separator which separates the liquor from the steam, whereby the liquor leaves through the bottom part of the separator while the steam leaves through the top. In order to keep fresh steam consumption to an absolute minimum, the evaporators are connected in series so that the subsequent steps are accomplished at a lower pressure and thus lower temperature and heated with the steam used in the previous step. The connection is in five steps, which are also termed effects. This way, fresh steam needs to be supplied only in step 1. A four-step system thus consumes only 30% of the heat as compared with an evaporator plant which makes use of only one step. A five and six-step system yield a consumption of 25% and 20%, respectively. In step 3 the mixed liquor is brought in and subsequently passes steps 4 and 5. Following step 5, the dry content of the liquor is over 35% and is termed semi-concentrated (or thickened) black liquor. The latter is heated in two tubular preheaters and six coil type preheaters before it is evaporated to the desired dry content in steps 1 and 2. Part of the concentrated liquor obtained is combusted in the soda recovery unit and the rest is used to raise the concentration of the stripping liquor. The utilized waste liquor is also mixed in the stripping liquor. The major part of the liquor vapor condensate is pumped to a wash-water tank, a minor part, however, is used in a column. The heat given off when the liquor vapor in step 5 condenses is used for hot water production by being heat exchanged with cold water that is heated to 50°C. The efficiency of the evaporation is lower than that of the previously described processes since this processes requires large quantities of steam for heating purposes.

Soda recovery unit

The organic substances in the black liquor released from the wood in the continuous digester are combusted in the soda recovery unit. Small quantities of chemicals such as sodium sulphate (about 30kg/tp) are added to the black liquor to replace the chemicals that were lost in the pulping process, before the liquor is sprayed into the soda unit through nozzles. The non-combusted substances in the concentrated liquor, are recovered in the melt at the bottom of the unit. Chemicals carried over with the gas exhaust (primarily sodium sulphate) are recovered in the electrostatic filter to be brought back to the black liquor. The heat generated during combustion is utilized to produce steam at a pressure of 3.6 MPa and a temperature of 430°C. The hot exhaust gases are utilized partly in order to reheat the combustion air and to heat the incoming feedwater from 110°C to 190°C. The recovered melt is cracked with steam before it falls into the melt mixer. Here, the melt is dissolved in the weak liquor from the causticizing department and this solution, in accordance with its color, is called green liquor. The green liquor is subsequently transported to the causticizing department where it is converted to the white liquor. The soda recovery unit is essentially a chemical reactor for recovering the processing chemicals present in the concentrated liquor. Energy efficiency is considered only once the safety and environmental requirements have been fulfilled. This explains the unit’s low exergy efficiency, which is a mere 36.3%.

Steam production unit

The production of steam from the combustion of the black liquor in the soda recovery unit does not suffice to meet the steam requirement of the mill, which is why a special steam production unit is installed. The bark and fuel oil are combusted and converted to steam at a very low exergy efficiency, for further comments see the total process below. As can be seen in Fig. 5.2, a bark equivalent of about 4.3 GJ/tonne paper was combusted in January 1979. The steam production unit consists of two steam boilers both of which can be oil fired and one which can be bark fired thanks to a special (Axon) furnace. As in the case of the soda recovery unit, the difference between energy and exergy efficiency is large, 88.4% as compared to 31.3%, respectively. This can be explained partly by the significantly lower exergy value (as opposed to the energy value) of the utilized outflows.

Turbine

The steam produced in the soda recovery unit and the steam production unit has considerably higher pressure and temperature than is necessary for the process. The steam can therefore by utilized in a back pressure turbine to generate electricity. The generated electricity constitutes approximately 30% of the mill’s electricity requirement. There are also pressure relief valves to make it possible to lower the pressure even while the turbine is not operating. A steam storage tank is used to level out the variations in production and consumption of steam. As a result of the large portion of steam that is being throttled (about 25%), the exergy efficiency is only 88%. In this case, more efficient regulation is recommended (compare cyclical regulation to throttling of fans and pumps).

Lime sludge reburning kiln and causticizing

In the causticizing department, the green liquor, which contains soda and sodium sulphide, is converted, causticized, to the white liquor. Sodium sulphide is used for pulp processing while the soda must be converted to sodium hydroxide before it can work effectively. This is done by adding lime to the green liquor.

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$$
(soda + lime + water → sodium hydroxide + calcium carbonate)

The lime and the green liquor are mixed in a so-called lime-slaker. The mixture then passes three causticizing vessels where the causticizing reaction takes place during mixing and at a temperature of 100°C. The so-called lime sludge (calcium carbonate sludge) is separated from the liquor in a white liquor clarifier and washed from the remaining chemicals in a lime-sludge washer and rotary vacuum filter before it is combusted in the lime sludge reburning kiln. A weak liquor builds up in the filter during the washing which is then used as the washing liquid in the lime-sludge washer. As it leaves the filter the lime sludge has a dry content of about 60%. Chemically the lime sludge is equivalent to limestone and is therefore converted to lime in the reburning kiln to be reused in the process. In this way, only the lime which is lost in the process has to be replaced. As the hot lime leaves the kiln at a temperature of about 1100°C, it is cooled to 200°C, at the same time preheating the combustion air. The exergy turnover in this process is, as we can see, relatively small. Because the reburning kiln is one of the few units to use oil (about 1200 MJ/tp), it attracts special interest from the point of view of efficiency.

Paper mill

The paper mill manufactures kraft liner which is built up of two layers. The bottom layer i made up of relatively roughly ground pulp, so-called base pulp (base stock), while the upper layer, which is thinner, is called top stock. The paper mill consists of the following units: stock preparation (also called beater section, crushing or grindning mill), wire part, press section and drying section, each of which fulfills the following functions:

Stock preparation. Between the sulphate factory and the paper mill is a pulp storage unit to which the (white) pulp water (the water from the drying of pulp to paper) is pumped in order to reduce fiber concentration. This mixture (4% pulp) is subsequently transported to the stock preparation department. Here, the fibers are ground, suitable chemicals added and the pulp diluted with the pulp water to form a mixture called stock with a fiber concentration of about 2.7%. Before the stock is pumped out to the wire part, it is diluted to a fiber concentration of 0.5% by briefly circulating the pulp water through the paper machine. The stock preparation department also processes waste paper fibers which are mixed into the base pulp.

Wire part consists of rollers, head boxes, suction boxes, etc. to construct the sheets and dewater the stock.

Press section consists of three rollers to press out the water under high pressure. This also improves fiber contact.

Drying section has the task of drying out the remaining water from the web by means of 96 steam-heated cylinders.

The paper machine is finished off with a calendering section and a reel-up, where the paper is reeled on a so-called reeling drum. The paper on the reeling drum is subsequently cut into suitable sizes in a slitter-rewinder and is then ready for delivery.

Nearly 100% of the supplied steam is used to dry the pulp to paper. The moist air thus obtained as a by-product is utilized to a minor extent to preheat the ventilation air. The supplied waste paper represents a fiber addition of about 0.2 tonnes/tp.

In a final product that contains about 0.93 tonnes of fiber, the extra fiber from the waste paper constitutes about 22%. If this extra fiber is removed from the process, the supplied raw material must correspondingly increase, that is, be multiplied by a factor of 1.28 to reach the same quantity of produced paper, i.e. 1 tonne.

The total process

Table 5.2 is a compilation of every subprocess and gives the quantitative and percentual energy and exergy losses relative to the entire mill. The total losses also include the unutilized outflows. Of the direct energy losses of the mill, the predominant losses are incurred in the soda recovery unit which accounts for more than half of the energy losses (column 1 and 2). Considerable losses are also incurred during screening, steam production and in the paper mill. If we also include the unutilized process flows (columns 3 and 4), the losses incurred in the soda recovery unit appear to be somewhat less. The steam production unit and the paper mill, which yielded considerable energy losses in the form of moist air and hot water now also play an important role.

Table 5.2. Energy and exergy losses in the pulp and paper mill

	Energy losses				Exergy losses			
Process:	Direct	%	Total	%	Direct	%	Total	%
Wood room	65	0.8	194	1.0	385	1.6	386	1.5
Continuous digester	169	2.0	169	0.8	270	1.1	270	1.0
Screening, etc.	1087	12.7	1087	5.4	570	2.3	570	2.1
Mixers, etc.	42	0.5	42	0.2	206	0.8	206	0.8
Evaporation	840	9.8	840	4.2	1039	4.2	1039	3.9
Soda recovery unit	4485	52.5	7228	36.2	9889	39.9	10549	39.8
Steam production unit	1271	14.9	3405	17.0	7616	30.8	8129	30.6
Turbine plant	3	0.0	3	0.0	742	3.0	742	2.8
Caustizing department	16	0.2	132	0.7	479	1.9	510	1.9
Paper mill	560	6.6	6875	34.4	3569	14.4	4125	15.6
Total	8538	100	19975	100	24765	100	25526	100

From the direct exergy losses (column 5 and 6) we also conclude that the soda recovery unit, the steam production unit, and the paper mill are the least efficient conversion processes. However, we see that the steam production unit now appears as a considerably larger source of loss than previously. This picture holds even when we compare the values in the last two columns which include the exergy losses in the unutilized process flows. From the column showing the direct exergy losses, we also see that exergy losses are almost equally distributed among the other processes. This is probably due to the fact that the mill is pretty well optimized in this regard. We also see a dramatic difference between the sum of the direct and total energy and exergy losses. In the case of energy, the unutilized outflows, i.e. the difference between the total and the direct losses, constitute 57% of the total losses but in the case of exergy, only 7%. The unutilized outflows are, essentially, a much smaller resource than energy calculation reveals. This constitutes the largest difference between an energy and an exergy treatment.

The losses in the paper mill can be partly justified by the considerable demands of the readymade product. This is also the final subprocess, which indicates that the all to large direct demands on the limiting of energy and exergy losses may result in an increased number of rejects which may result in even higher total losses for the entire factory. The immediate efforts to increase exergy efficiency should therefore be directed at the soda recovery unit and the steam production unit. Before we examine these in more detail, let us see how the losses in the unutilized process flows are distributed in terms of energy and exergy.

In Table 5.3 we see that the exergy losses are predominantly exhaust gases and damp air which, of course, are strongly linked to the soda recovery unit and steam plants. The temperature of the exhaust gases varies between 145°C and 170°C. This makes the exhaust gases interesting from the point of view of electricity production (Horio 1982). However, of immediate interest is the preheating of air and fuel. The temperatures of the damp air and water are so low that they can only be applicable for space heating purposes or possibly as a heat source in a heat pump system.

Table 5.3. Unutilized outflows

Unutilized outflows:	Energy	%	Exergy	%
Damp air	4680	40.9	479	27.2
Flue gas and soot blowing	4993	43.7	1204	68.4
Water (30-55°C)	1764	15.4	78	4.4
Total	11437	100	1761	100

Thus, an exergy calculation for the mill unequivocally reveals that the soda recovery unit and steam production unit ought to be made more efficient. That this should be possible to accomplish can also be seen by looking at the combustion efficiencies of these two, which are a mere 27% and 31%, respectively. The disparity between the exergy price and capital costs, however, indicates that the calculation method ought to be taken further, for example, using thermoeconomic methods (Wall 1985). Thus, altering the steam production unit, for example, to replace oil-firing with bark-firing, can be cost-effective in spite of the higher energy and exergy losses.

Let us now treat the entire factory as a process of conversion where investments like wood yield paper and liquid resin, Fig. 5.2 (the ice is negligible). We see that about 47% of the incoming exergy remains in the final product. Of the exergy content of the incoming wood, about 56% remains in the manufactured paper. This value can be compared with the yield, 57%, measured as dry substance. For the process as a whole, the result can be a nearly double exergy yield from the wood. At present, it is impossible to say how this can be accomplished. Perhaps in the future, bacteria and fungi will be able to decompose the wood to a pulp more efficiently than current-day processes. A first step towards more exergy-efficient processes would be to channel efforts to improve the mill in accordance with the exergy losses. However, in the short run, research efforts ought to be directed primarily to improve the soda recovery unit. This study is concerned with exergy and does not deal with other aspects such as practical and economic which are also relevant. Other studies are needed to provide additional justification to the proposed measures.

6. A STEEL PLANT

The data for this study is based on a 1978 study by Jan Fors and Rune Hardell of energy use in three steel plants, interviews with chief of operations at the Halmstad steel mill, Roland Myrgård, and current litterature in the field (Flinn 1963, Hiwatashi 1981, Nishikawa 1980, Fett 1982, Sharp 1967 and Sims 1962). The energy calculations in this study differ from those of Fors and Hardell in terms of the chemical energy in the material that has not been combusted. Moreover, different methods have been used for calculating the heat content which yields values for the exhaust heat, for instance.

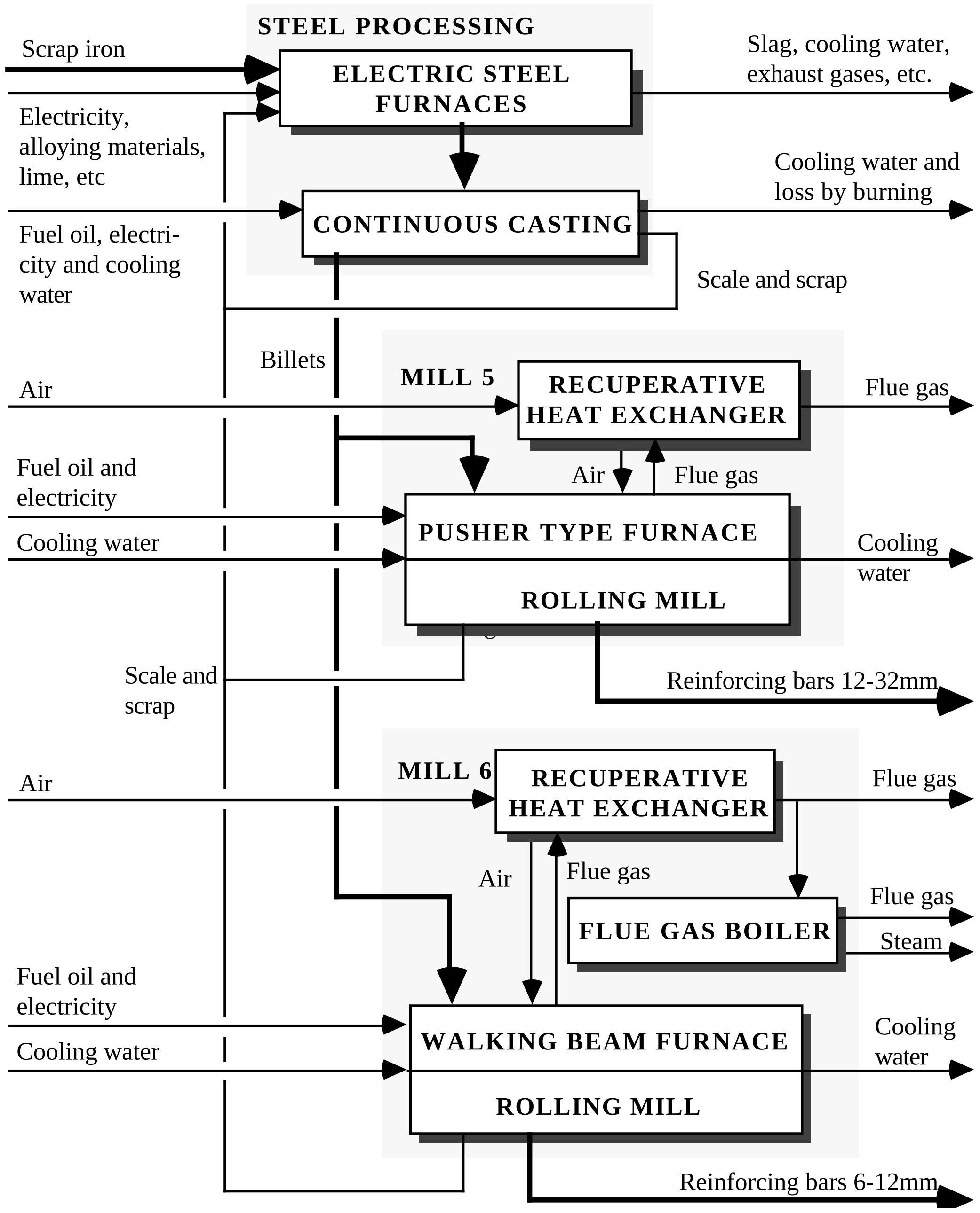

Fig. 6.1. A steel plant

Fig. 6.2. Exergy flow in a steel plant

The Halmstad steel plant has an annual production capacity of approximately 280 000 tonnes of reinforcing steel (this is valid for the actual year under study (Fors 1978)). The present study deals with the steel mill and with the rolling mill. The raw material is melted in two electric steel furnaces with a 50 tonnes capacity each and is then cast in two continuous casting machines with three continuous runs each. The billets are rolled in two rolling mills (mill 5 and 6) to bars and wires of circular crossections of 5 to 32 mm. (The data is based on monthly production in March 1976). Figure 6.1 gives a schematic illustration of the process. The material flow in kg/tonne of produced reinforcing steel (kg/tr) and the energy and exergy flows in MJ/tr of the mill are given in tables in Appendix 2 for every subprocess. Note that the exergy value given for the steel only represents the so-called “physical quality” of the steel in relation to the reference conditions selected. That is, the work that could be theoretically extracted if we could operate a machine in which steel is converted to the metal oxides and other reference condition substances. The exergy value does not include other properties that are a measure of quality such as ductility and corrosion restistance. The exergy value is more linked to the manufacturing of the product at hand than with its properties. The exergy value can be said to give the minimum theoretical resource requirement for manufacturing the product at the assumed reference conditions. By comparing in terms of exergy two different methods of manufacturing the same end-product, we can establish which method is thermodynamically most efficient.

Figure 2 illustrates the exergy flow in the steel plant. The widths of the illustrated flows are proportional to the exergy content. Total inflow is approximately 12 700 MJ/tr and the total outflow of reinforcing steel is approx. 6 800 MJ/tr. The unutilized outflows are equivalent to approx. 1 000 MJ/tr which yields an exergy efficiency of 54%. This diagram also provides a good overall picture of the mill’s resource flows of electricity, fuel oil, heat and steel.

Electric steel furnaces

Scrap iron is melted and, in order to obtain the right chemical composition, alloying materials are added. Lime and fire-resistant material as well as graphite from electrodes are consumed in the process. Large quantities of cooling water are used to maintain the furnace at a low and stable temperature. Scrap iron and electricity represent the largest exergy flows. The cooling water accounts for the largest material flow, about 17m^3/tr. The readymade steel constitutes the predominant outflow, and through its high temperature of about 1 650°C it also contains a large quantity of thermal energy. By comparing the inflows and outflows, we can calculate the energy and exergy efficiencies, see Appendix 2. The exergy efficiency is lower than the energy efficiency, 88.5% as compared to 97.7% which is due to the fact that the heat in the readymade steel has a lower exergy than energy value, 1 662 MJ/tr energy as compared to 1 189 MJ/tr exergy, which is also shown in Fig. 6.2.

The chemical energy content of the steel is 7.55 MJ/kg. The chemical exergy value of the scrap iron has gone up from 6.45 to 6.84 MJ/kg in the readymade steel, which represents a small change in exergy but a very important change in quality.

Slag (292 MJ/tr) and exhaust gases (265 MJ/tr) from the molten iron represent the largest unutilized (waste) flows. The temperature of the exhaust gases varies between 500°C and 1 500°C. The cooling water represents a substantial energy flow, 356 MJ/tr, but because of its low temperature, 30°C, is of very little interest in terms of exergy, 3 MJ/tr. The thermal exergy content is less than 1% of the thermal energy content since the temperature is only 5°C higher than ambient temperature. The readymade steel is tapped on a ladle and tranported to be cast.

Continuous casting

The solidifying steel is cooled with water as it is cast and subsequently cut into suitable lengths to billets. As the steel is cooled, the thermal energy and exergy in the hot billets is lost. The hot billets are placed on a cooling bed, where the temperature drops from about 850°C to about 450°C. Because in the later stages of processing, the steel is handled with magnets, the temperature must be lowered to well below Curie temperature, which is about 770°C. During the cold season of the year, this heat is used for space heating. From the cooling bed the billets are placed on wagons outside awaiting transport to the rolling mill. As a rule, the temperature drops to somewhere between 100°C and the prevailing outdoor temperature before the billets are transported to the rolling mill. This process is illustrated in Fig. 6.2 as a decrease in the outflow from the continuous casting.

Pusher type furnace (mill 5)

The rolling mill consists of two mills. The heavier steel is rolled in mill 5 into bars between 12 and 32 mm in diameter and in mill 6 to bars and wires between 6 and 12 mm in diameter. Large quantities of cooling water are used in the rolling mill, too, about 2 900 kg/tr. No measurements have been made of how this water is being used in the rolling mill, which is why I have chosen to illustrate this separately.

The rise in temperature is about 15°C and the change in energy and exergy (content) is about 183 MJ/tr and 5 MJ/tr, respectively. About two thirds of the billets are rolled in mill 5. The billets are heated to about 1 150°C prior to rolling.

Heating takes place in such a way that the billets are successively pushed against the hotter part of the furnace. The composition, by weight, of the exhaust gases is 73% nitrogen, 10% oxygen, 12% carbon dioxide and 5% steam. The losses consist of heat given off to the surroundings and in the exergy calculation also as losses when the chemical exergy in the fuel oil is converted to heat. The efficiency of the furnace, defined as heated steel divided by utilized fuel (oil and air) is about 74% for energy and about 35% for exergy. This leaves plenty of room for technical improvement as shown by the low values of exergy efficiency.

Recuperative heat exchanger (mill 5)

Part of the exhaust heat from the pusher type furnace is used to preheat the combustion air from outdoor temperature to about 330°C. (Note that the direction of the current for this process is reversed in Fig. 6.2, i.e. from right to left). It is assumed that the temperature of the flue gas entering the recuperative heat exchanger is 850°C, and that leaving the heat exchanger 500°C, respectively, since exact data is not available. The efficiency, defined as absorbed heat divided by heat given off is 73% and 34%, respectively. The exergy efficiency is very low despite the high energy efficiency.

Rolling mill (mill 5)

The hot billets are now rolled to reinforcing bars 12-32 mm in diameter. Scrap and scale is returned to the electric steel furnaces. The temperature of the readymade steel is assumed to be 850°C. The losses are primarily heat lost to the surroundings as a result of the cooling and the internal friction losses when the billets are rolled. The heat of the finished reinforcing steel, 191 MJ/tr, is lost to the surroundings through cooling.

Walking beam furnace (mill 6)

The reinforcing steel with fine crossections of 6-12 mm is rolled in mill 6. The billets are fed in gradually into the hotter part of the furnace. If we compare this with a pusher type furnace, we find that on the whole the efficiency of both furnace, is very similar. A part of the exhaust heat is utilized in the recuperative heat exchanger to preheat the combustion air to about 350°C.

Recuperative heat exchanger (mill 6)

The energy and exergy efficiencies differ considerably in this heat exchanger, too, about 55% and 28%, respectively. (The direction of the flow in Fig. 6.2 is reversed in this case as well.) This is typical for all heat exchangers and is due to the fact that passive heat transfer generally causes large exergy losses. However, in this case, some of the exhaust heat is also utilized in a flue gas boiler.

Flue gas boiler (mill 6)

Some of the exhaust heat from the walking beam furnace is also used via the recuperative heat exchanger for steam production in a flue gas boiler. Whenever data is not available, this part is assumed to be 60% of the exhaust flow from the recuperative heat exchanger. The steam thus generated is transported to a boiler dome to be further used for domestic hot water heating, and to some extent, as industrial steam in the rolling mill.

Rolling mill (mill 6)

The cooling after rolling of a total of 1 000 kg of steel at 85°C in both rolling mills yields, as we can see, an energy loss of 558 MJ, see Appendix 2, and an exergy loss of 311 MJ.

The total process

The energy and exergy losses of each subprocess and of the entire plant are shown in Table 6.1. The total losses consist partly of direct losses in the subprocess itself and during cooling, and partly of unutilized flows. Of the direct energy losses (column 1 and 2), the continuous casting, the first cooling stage, both rolling mills and the final cooling appear as the largest. Together, these account for 2 620 MJ/tr or 77.7% of the direct energy losses. If we include the unutilized flows (columns 3 and 4), the electric steel furnaces and the continuous casting emerge as the largest sources of loss. More or less the same picture is maintained when we calculate the exergy losses. Moreover, both furnaces contribute considerable exergy losses. These furnaces also consume fuel oil which is used by the mill. It would be possible to utilize the exhaust from all of the furnaces using conventional technology so that the exhaust temperature is lowered to below 200°C before it leaves the mill (Hiwatashi 1981). All of the heat losses could also be utilized for electricity production in a low temperature turbine plant (Horio 1982). A simplified compilation of the losses of the mill can be made in order to further point out the differences between an energy and an exergy treatment, Table 6.2. In the energy calculation, the losses in the unutilized outflows appear most important beside the direct losses in the process itself. An important difference is that in the exergy calculation, the direct losses constitute the entirely dominant losses. The unutilized outflows, such as waste heat and cooling losses are less important.

Table 6.1. Energy and exergy losses in the steel plant

	Energy losses				Exergy losses			
Process:	Direct	%	Total	%	Direct	%	Total	%
Steel process								
Electric steel furnaces	247	7.3	1462	23.8	1172	24.2	1859	32.0
Continuous casting	517	15.3	1217	19.8	989	20.4	1019	17.5
Cooling	611	18.1	611	10.0	353	7.3	353	6.1
Mill 5								
Pusher type furnace	175	5.2	175	2.9	556	11.5	556	9.6
Recuperative heat ex.	85	2.5	585	9.5	144	3.0	335	5.8
Rolling mill	481	14.3	494	8.0	436	9.0	446	7.7
Mill 6								
Walking beam furn.	131	3.9	131	2.1	352	7.3	352	6.1
Recuperative heat ex.	104	3.1	179	2.9	109	2.3	132	2.3
Flue gas boiler	10	0.3	84	1.4	8	0.2	26	0.4
Rolling mill	420	12.5	427	7.0	391	8.1	397	6.8
Mill 5 and 6								
Cooling water			183	3.0			5	0.1
Cooling	591	17.5	591	9.6	329	6.8	329	5.7
Total	3372	100	6139	100	4839	100	5809	100

Earlier in this paper, we mentioned losses in connection with cooling of the hot billets. However, these losses should be examined more closely since the preheating prior to rolling is a direct function if the earlier cooling stage. We could argue that when the billets are allowed to cool, the total losses should also include the total heating cost later in the process. The total loss during cooling is thus 2257 MJ/tr (exergy) or about 39% of the total losses of the mill. This indicates that the casting-rolling process ought to be continuous. However, a completely continuous process is usually impossible to achieve. Instead, various alternatives should be developed, for example, to prevent heat emissions or to utilize the heat for other purposes. Today’s steel plants already are attempting to keep the time between the casting and rolling to an absolute minimum. This particular measure ought to be further examined with regard to the large savings, particularly of oil, this could mean. The exergy flows in the heating of steel have also been studied at Kyshu University and by the Nippon Steel Company (Nishikawa 1980), whose conclusions are in good agreement with this study. Oil consumption alone accounts for over 15 000 m^3/yr which, at an oil price of SEK 2 000/m^3, is equivalent to SEK 30 million in operating costs alone. There are thus good economic reasons to investigate whether better ways can be found of re-allocating these funds within the process.

Table 6.2. Energy and exergy losses

	Energy losses	%	Exergy losses	%
Direct losses	2170	35.3	4157	71.6
Cooling losses	1202	19.6	682	11.7
Unutilized outflows	2767	45.1	970	16.7
Total	6139	100	5809	100

7. SPACE HEATING

The most common energy conversion process in Sweden is the conversion of low-temperature heat. Today, this takes place independently of the industrial processes, under entirely different conditions and objectives. The difference in efficiency is thus very substantial. Space heating presently accounts for 40% of Sweden’s energy consumption. Space heating is the largest single energy user in Sweden. At the same time, it represents the largest exergy loss in the country, but also the simplest to improve. Let us first see what space heating actually is about by looking at the whole picture from a scientific point of view. We maintain the temperature of a system with defined boundaries, a building, at about 293K (=20°C) in surroundings at about 273K. If we view the process in this way, we can also see how relatively small the temperature increase really is, the task is to maintain the temperature at about 7% over ambient temperature.

Many people today are very pleased to assert that the efficiencies of certain space heating systems are nearly 100%. They claim that the efficiency of an oil-fired boiler is 85% and that of electric heating, 100%. This may be true, but the maximum value of efficiency thus defined is about 1500%. Thus, a heat pump can supply more thermal energy than it consumes as work in the form of oil or electricity. However, this relationship is never mentioned (to my knowledge). This way of thinking often projects an incorrect picture of a space heating system. The concept of exergy offers a better way to describe a system and it means, among other things, that the maximum possible efficiency would never exceed 100%. Let us now take a closer look at the space heating of a house.

Assume that we can maintain a temperature of 20°C in a house that is located in surroundings at a lower and varying temperature. The energy requirement for heating the house will then vary more or less directly with the difference between indoor and outdoor temperature. The effects of wind and humidity are not considered in this case. At the same time, the exergy value of the supplied heat also varies in relation to the outdoor temperature as follows:

$$E = Q(T-T_o)/T \tag{7}$$

where T is the indoor temperature (293K), T_o the varying outdoor temperature, and Q the heat quantity supplied to the house. We recognize the factor $(T-T_o)/T$ as the so called Carnot coefficient, see Eq. (1). At an outdoor temperature of 0°C, this will be about 6.8%. With data on how the outdoor temperature varies throughout the year, we can calculate the real exergy requirement during the heating season. We can then obtain the following results, valid for 1975 (Wall 1981), see Table 7.1.

Table 7.1. Mean annual temperature T_o, minimum five-day mean temperature T_{min}, number of heating days d, exergy value E/Q, portion of the population X and relative exergy value X·E/Q in 1975.

Representative town[a]	T_o°C	T_{min}°C	d days	E/Q%[b]	X%	X·E/Q%
Umeå	4.0	-11.0	277[c]	6.72	9.4	0.632
Östersund	4.2	-9.2	283	6.27	8.5	0.533
Karlstad	7.7	-4.4	235	5.00	9.9	0.495
Stockholm	8.4	-3.2	230	4.84	24.0	1.160
Jönköping	7.9	-3.6	237	4.82	17.3	0.834
Göteborg	9.3	0.3	226	4.00	16.6	0.664
Malmö	9.1	-1.6	225	4.54	14.3	0.649
				Total	100.0%	4.97%

[a] The country is divided into areas according to: (the letters represent counties) Umeå: BD, AC, Y, Östersund: X., Z, W, Karlstad: S, T, U, Stockholm: A, B, C, D, Jönköping: E, F, G, H, I, R, Göteborg: N, O, P, Malmö: K, L, M.

[b] Calculated at an indoor temperature of 20°C and a diurnal temperature variation of 4°C.

[c] Value refers to Luleå.

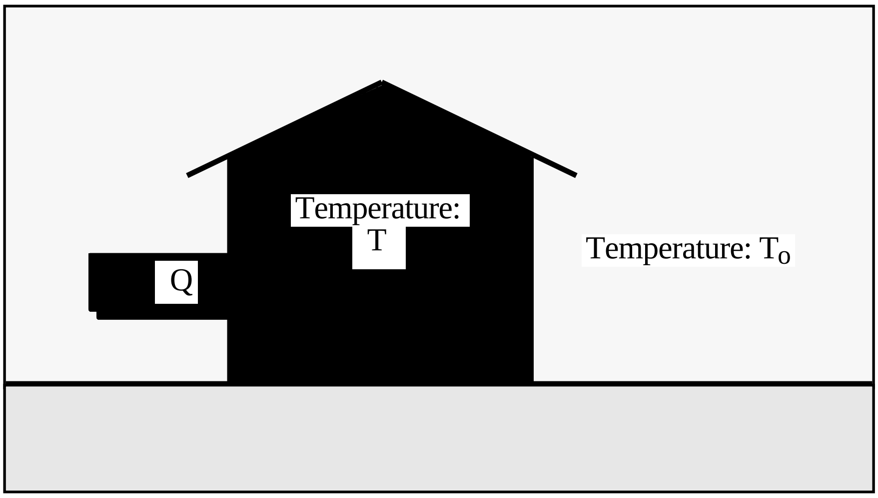

Fig. 7.1. Indoor temperature T in a house at ambient temperature T_o is maintained by a heat flow Q, which exactly counterbalances the heat flow to the surroundings.

The urban areas with colder temperatures have higher exergy values, since warm house heat represents a higher contrast to the surroundings. On the other hand, more energy is required for space heating. Since energy consumption is concentrated to densely populated areas, a weighted average value for all of Sweden can be calculated at about 5%. This result can be interpreted is such a way that the space heating requirement in terms of exergy constitutes only about 5% of the energy requirement. The above-mentioned oil-fired boiler thus yields an exergy efficiency of 4.3% and the electric heater 5%. Assuming an ideal heat pump, the energy consumption for space heating could theoretically be reduced to one twentieth. This enormous waste of resources, which results from an inadequate technology more than justifies a stronger commitment to limit space heating requirements by means of such measures as insulation and sealing of joints. Today’s deplorable space heating technology, which results in a huge energy use and environmental destruction, is worse and more dangerous than when Englishmen wrecked their forests for making fire-wood during the 18th century. New efficient space heating systems such as heat pumps and better building construction and materials can save considerable resources of which environmental resources are not least important, e.g., forest destruction due to acid rain.

8. ENERGY AND EXERGY PRICES

The choice of energy source for industrial and other uses is primarily governed by prices. The energy conversion system thus created places corresponding demands on the energy supply system. Sometimes, these systems are shown to be uneconomical with time or in a long-term perpective, i.e., prices are incorrect or insufficient as a basis for planning. One example of this is when prices are set based on short-sighted political assessments or on insufficient knowledge of the resource in question and the consequences of its use. It is therefore important to find a sounder method for price setting. Prices based on exergy values could be designed so as to benefit resource-saving and efficient technology. Large exergy losses should also mean large economic losses. The prices of physical resources ought to be set more in relation to the physical value of these resources, i.e., exergy.

This chapter explains the differences between the price setting of several common energy sources and their respective exergy values (Liljenstam et al. 1982). All prices are valid for Göteborg in spring 1982 and include taxes.

Electricity

Electrical energy can be treated as totally converible to work. The energy price is therefore also the exergy price. The price of electricity varies considerably, among other things, with respect to the maximum output and consumption (fixed and variable cost). However, the varation between small consumers such as various categories of households, are relatively minor. The average cost to a subscriber using electricity for space heating is about SEK 0.23/kWh, and to a subscriber without electric heating about SEK 0.27/kWh. This yields an energy and exergy price of about SEK 64/GJ and SEK 75/GJ, respectively. To large subscribers, such as industries, the cost is often significantly lower.

Gasoline and diesel

Gasoline consists mainly of octane C_8H_{18} for which the exergy content is calculated at about 94% of the energy value. Regular gasoline (44.2 MJ/kg) is assigned an energy price of SEK 114/GJ and an exergy price of SEK 121/GJ which corresponds to a price of approx. SEK 3.68/l. Premium gasoline (44.0 MJ/kg) has an energy price of SEK 118/GJ and an exergy price of SEK 126/GJ which corresponds to a price of SEK 3.80/l.

The exergy content of diesel (42.7 MJ/kg) is assumed to be 104%, which is valid for kerosene. (The exergy value is higher than the energy value since, among other things, the partial pressure of carbon dioxide is included in the exergy calculation): At a price of SEK 2.09/l, the exergy and energy prices are SEK 59/GJ and SEK 56/GJ, respectively. A kilometer tax on motor vehicles should be added to these costs.

Fuel oil

The exergy content of fuel oil is assumed at 97%, which is valid for the havier oils. The following table is then obtained for the prices of several common classes of oil. The energy and exergy prices vary between SEK 43/GJ and SEK 44/GJ for the heavier oils, and SEK 56/GJ and 58/GJ for the lighter oils.

Table 8.1. Energy and exergy prices of several common fuel oils

Fuel oil no.	Heating value (MJ/kg)		Price (SEK/GJ)	
	Energy	Exergy	Energy	Exergy
I[a]	42.8	41.5	56	58
III	41.7	40.4	47	48
IV	41.4	40.2	46	47
V	41.4	40.2	43	44

[a] Oil no. I is used for domestic oil-fired boilers since it is liquid at room temperature.

Town gas

According to the Energy Authority of Göteborg, town gas consists of 65% hydrogen, 20% carbon dioxide, and other substances. The energy and exergy content of town gas can be calculated at 92.2 MJ/kg and 75.5 MJ/kg, respectively, i.e. the exergy content constitutes about 82% of the energy. Considering that prices are determined on the basis of such factors as output requriements and energy needs, and assuming an annual consumption of 200 MWh, we get an energy price of about SEK 63/GJ. The exergy price will thus be SEK 77/GJ.

Coal

The exergy content and price of coal varies for each coal type, see Table 8.2. As we can see, the variations are minimal and both the energy and the exergy prices are around SEK 20/GJ.

Table 8.2. Energy and exergy prices of several common types of coal

Coal type	Heating value (MJ/kg)		Price (SEK/GJ)	
	Energy	Exergy	Energy	Exergy
Sorted (8-30 mm), sulphur cont. ≤ 0.6 %	29.7	29.4	21	21
Sorted (0-30 mm), sulphur cont. ≤ 0.6 %	23.8	23.6	20	20
Unsorted, sulphur cont. ≥ 0.6 %	27.2	26.4	18	19

Wood products

The fuel value of wood products varies considerably depending on the water content. In the case of wood with a 50% water content, the energy and exergy value is calculated at 12.4 MJ/kg and 12.1 MJ/kg, respectively. These values are valid when the water vapor used is condensed in the process. It is difficult to calculate a relevant price due to the relatively small amounts of wood that are sold for space heating purposes. On the other hand, the prices of woodpulp are fixed. The price may vary between SEK 110-160/m^3 depending on the wood type. These prices refer to stacked wood with bark. Recalculating for the real volume of a whole debarked trunk (by a factor of 0.83), we get a price per kg (density 450 kg/m^3) of SEK 0.2 - 0.3/kg. The energy and exergy price will thus be SEK 16 - 24/GJ.

Paper with a water content of 40% yields an energy and exergy value of 15.6 MJ/kg and 15.0 MJ/kg, respectively. At a 10% water content, these values are 23.4 MJ/kg and 22.5 MJ/kg, respectively. In this report the water content of waste paper is assumed at 25%, which yields the values 19.4 MJ/kg and 18.7 MJ/kg. The price of waste paper varies considerably. The Jönköping municipality sells its reclaimed waste paper at SEK 0.35/kg, while the municipality of Göteborg sells its at SEK 0.21/kg. The price will thus vary from SEK 11 - 18/GJ (energy) and from SEK 11 -19/GJ (exergy).

The water content of wood powder varies between 3% and 15% which results in an energy value of between 24.1 MJ/kg and 21.2 MJ/kg and and exergy value of between 23.4 MJ/kg and 20.5 MJ/kg. Assuming a moisture content of 10%, the energy value is 22.4 MJ/kg and the exergy value 22.7 MJ/kg. The price is about SEK 0.73/kg which yields an energy price of SEK 33/GJ and an exergy price of SEK 34/GJ, respectively.

District heating

The exergy of a given quantity of district heat can be calculated as:

$$E = Q\,(1 - T_{outdoor}/[T_{supply} - T_{outdoor}]\ \ln[T_{supply}/T_{return}]) \qquad (8)$$

The supply and return temperatures within the district heating system in Sweden are regulated with respect to the outdoor temperature. The supply temperature is maintained at about 85°C at outdoor temperatures above +2°C and is subsequently raised in inverse proportion to the outdoor temperature, up to 120°C at an outdoor temperature of -20°C. The exergy content will thus vary with the outdoor temperature according to Fig. 8.1 below. For Göteborg, the mean exergy content is calculated at about 17% of the total heat quantity required for the heating season. The district heating subscriber in Göteborg is charged a fixed rate plus an estimated energy rate. Under conditions similar to the case of town gas, the energy price is SEK 58/GJ and the exergy price SEK 340/GJ. We see that the exergy price is thus 6 times that of energy.

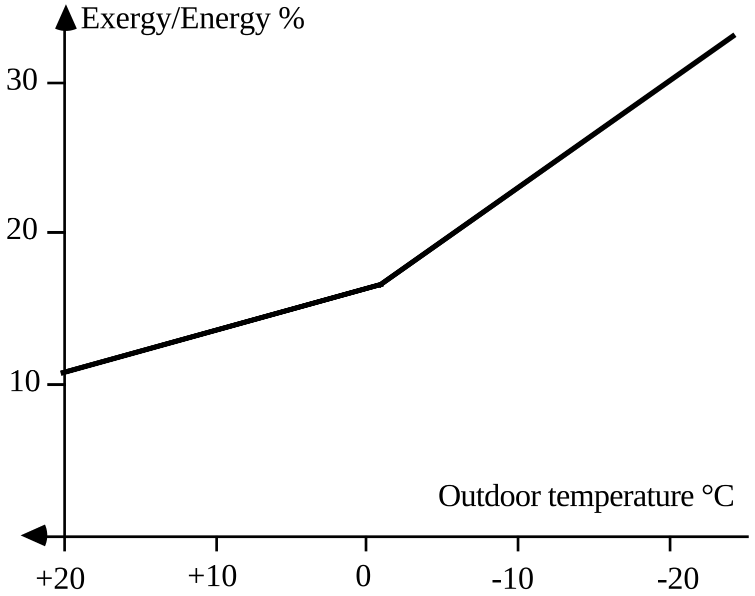

Fig. 8.1. The relationship between exergy and energy for district heating at different outdoor temperatures

Conclusion

We now obtain the following energy and exergy prices for the energy sources under study, see Table 8.3. The highest energy price is that of gasoline, which is a refined fuel with special areas of use. The lowest energy price is that of paper, which is also probably the most expensive and least efficient to handle as fuel. The prices of coal and wood products are low. The differences in energy and exergy prices are small for all the energy sources except district heating. The district heating subscriber pays much more for exergy than other energy users. In many cases, the consumer could reduce his heating bill by instead using a heat pump to produce heat. The current price situation is such that it is cost-effective to produce heat with the aid of heat pumps rather than subscribe to district heating, but it is also cost-effective to use heat pumps in district heating systems. In this case, too, it should be expected that the price will be adapted with respect to this condition. A conscientious energy policy could speed up development towards efficient resource-saving technology by ensuring exergy, rather than energy use.

Table 8.3. Energy and exergy prices of several common energy forms

Energy form	Energy price SEK/GJ	Exergy price SEK/GJ
Electricity	64-75	64-75
Gasoline	114-118	121-126
Diesel	59	56
Fuel oil no. 1	56	58
Fuel oil no. 3-4	43-47	44-48
Town gas	63	77
Coal	18-21	19-21
Fire wood	16-24	16-24
Paper	11-18	11-19
Wood powder	33	34
District heating	58	340

9. GENERAL CONCLUSION

The main lesson of the present study is that, of the studied processes, the exergy treatment reveals heating processes as highly inefficient. This is almost always the case for exergy calculations and is due to the fact that the exergy value of heat is often much lower than its energy value, particularly at temperatures close to ambient temperature. Thus, processes using higher temperatures, such as melting of iron, are better since the exergy value increases with the temperature above ambient temperature. Wastewater at one or two degrees above ambient temperature has, for all practical purposes, no exergy value at all.

At the pulp and paper mill, the soda recovery and the steam production units appeared as the least efficient subprocesses. Within the framework of the earlier mentioned demands of the soda recovery unit, it should be possible to develop better technology for these subprocesses. Perhaps in the future, bacteria will be able to decompose the wood substances and give us a more efficient technology. An ideal process, which incurs no losses whatsoever, would effect about 50% reduction in the use of current resources. Today’s pride in the paper and pulp industry over the fact that certain mills do not require external fuel supply such as oil is entirely justified. In the future, when the mill will become a supplier of paper as well as fuel and electricity, there will be even more reason to boast.

The steel industry’s energy and exergy losses primarily refer to the electric steel furnaces and continuous casting. Just as in the pulp and paper mill, the exergy value of the unutilized flows will be significantly lower than the energy value. It may also be noted that efficiency at the steel mill in question has been improved by the replacement of two furnaces with one, built for a higher capacity. Technology ought to be developed to prevent heat losses between casting and rolling.

Compared to industrial processes, space heating appears to be highly inefficient. One explanation for this may be that the demand for profitability in industry results in a better management of resources. There is often less emphasis on profitability in non-industrial processes. Moreover, the ability of the private consumer to influence his own space heating costs is limited. Efficiencies below 5% for present day space heating systems leave plenty of room for technical improvements, e.g. heat pumps. The efficiency is even less for example, if we examine the space heating system: nuclear - electric heat. The chain of energy conversion nuclear - electricity - heat yields an efficiency of about 1.5%. If we also take into account the fact that only a minor part of uranium’s exergy content is utilized in today’s light water reactors, the efficiency is extremely low. System efficiencies on this order ought to be avoided in the future.

The price of various energy sources is determined, among other things, by the energy value. Calculated in terms of exergy, the price of district heating is about 5 times too high. Consequently, the development of efficient heat production technology such as heat pumps is highly commendable. In the long run, this must also influence district heating prices. A more exergy conscious price setting of various energy sources would help advance technological development towards resource-saving and efficient technology.

In conclusion, it should also be mentioned that the application of the exergy concept provides information for long-term planning of resource management. Today, there is competence and experience for short-term planning. Unfortunately, this is not the case for longer-term planning. This often obstructs development of new efficient technology. The concept of exergy is thus a worthwhile complement to present-day planning instruments.

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Appendix 1. Material, energy and exergy flows in a paper mill

Wood room	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Wood -16°C	2.67	33430	87.3	32660	87.7
Bark -16°C	0.44	4357	11.4	4316	11.6
Ice -16°C[a]	0.70	-306	-0.8	25	0.1
Electricity	-	225	0.6	225	0.6
Water 50°C	5.43	569	1.5	22	0.1
Total:	9.24	38275	100	37248	100
Outflow:					
Chips 25°C	2.67	33674	88.0	32587	87.5
Bark 25°C	0.44	4407	11.5	4275	11.5
Water 30°C	6.13	129	0.3	1	0.0
Total:	9.24	38210	99.836863		99.0
Loss	0	65	0.2	385	1.0
Unutilized outflow	6.13	129	0.3	1	0.0
Efficiency			99.8		99.0

[a]The negative energy values are due to the reference temperature which is assumed to be 25°C. (Please note that this temperature is assumed to be 0°C in the energy study to which we refer (Fors and Nord 1980).)

Continuous digester	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Chips	2.67	33674	38.8	32587	40.6
White liquor 85°C	1.97	3946	4.5	2875	3.6
Liquor 70°C	13.80	47398	54.6	44099	55.0
Steam[a]	0.64	1717	2.0	502	0.6
Electricity	-	153	0.2	153	0.2
Total:	19.08	86888	100	80216	100
Outflow:					
Pulp & liquor 70°C	10.64	65665	75.6	62401	77.8
Stripping liquor 145°C	6.29	20949	24.1	17531	21.9
Water 118°C	0.27	105	0.1	14	0.0
Water 25°C	1.88	0		0	
Total:	19.08	886719	99.8	79946	99.7
Loss	0169		0.2	270	0.3
Unutilized outflow	1.3	0		0	
Efficiency			99.8		99.7

[a]0.25 tonnes/tp 0.5 MPa, 175°C, 0.12 tonnes/tp (flashed steam) 130°C, 0.27 tonnes/tp 1.3 MPa, 205°C.

Screening, washing and refining	Weight:	Energy		Exergy	
	tonnes/tp	MJ/tp	%	MJ/tp	%
Inflow:					
Pulp & liquor 70°C	10.64	65665	96.5	62401	99.0
Water 74°C	8.99	1840	2.7	129	0.2
Steam 1.3 MPa, 205°C	0.07	178	0.3	57	0.1
Electricity	-	378	0.6	378	0.6
Total:	19.70	68061	100	62965	100
Outflow:					
Pulp 55°C	5.90	19576	28.8	18296	29.1
Liquor 70°C	13.80	47398	69.6	44099	70.0
Total:	19.70	66974	98.4	62395	99.1
Loss	01087	1.6	570	0.9	
Unutilized outflow	0	0		0	
Efficiency			98.4		99.1

Mixers and heat exchangers	Weight:	Energy		Exergy	
	tonnes/tp	MJ/tp	%	MJ/tp	%
Inflow:					
Stripping liquor 145°C	6.29	20949	51.0	17531	48.0
Heavy black liquor 102°C	1.52	18294	44.5	16920	46.3
Waste liquor 55°C	0.47	2209	5.4	2028	5.6
Water 1°C	3.44	-347	-0.8	31	0.1
Total:	11.72	41105	100	36510	100
Outflow:					
Mixed liquor 76°C	7.84	38058	92.6	34436	94.3
Steam[a]	0.37	943	2.3	261	0.7
Water 55°C	3.44	432	1.1	21	0.1
Soap 76°C[b]	0.07	1630	4.0	1586	4.3
Total:	11.72	41063	99.9	36304	99.4
Loss	042	0.1	206	0.6	
Unutilized outflow	0	0		0	
Efficiency			99.9		99.4

[a] 0.12 tonnes/tp 130°C and 0.25 tonnes/tp 109°C

[b] Corresponds to a production of 45 kg of resin oil per tonne of pulp.

Evaporator plant	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Mixed liquor 76°C	7.84	38058	94.2	34436	96.9
Steam 0.5 MPa, 175°C	1.28	3448	8.5	948	2.7
Water 108°C	0.02	8	0.0	1	0.0
Water 1°C	11.47	-1155	-2.9	102	0.3
Electricity	-	50	0.1	50	0.1
Total:	20.61	40409	100	35537	100
Outflow:					
Heave black and black liquor 102°C	2.90	34903	86.4	32282	90.8
Waste liquor 55°C	0.47	2209	5.5	2028	5.7
Condensate 52°C och 93°C	5.77	1257	3.1	141	0.4
Water 50°C	11.47	1200	3.0	47	0.1
Total:	20.61	39569	97.9	34498	97.1
Loss	0840		2.11039	2.9	
Unutilized outflow	0	0		0	
Efficiency			97.9		97.1

Soda recovery unit	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Black liquor 102°C	1.38	16609	89.9	15362	94.9
Weak liquor 55°C	1.93	730	3.9	439	2.7
Water 110°C	2.97	972	5.2	117	0.7
Steam 1.3 MPa, 205°C	0.03	89	0.5	29	0.2
Electricity	-	121	0.6	121	0.7
Air 25°C	8.9	0		0	
Na_2SO_4	0.03	152	0.8	118	0.7
Total:	15.21	18673	100	16186	100
Outflow:					
Steam 3.6 MPa 420°C	2.54	7620	40.8	2956	18.3
Bottom blow 255°C	0.34	338	1.8	93	0.6
Green liquor 90°C	2.43	3487	18.7	2588	16.0
Exhaust gas 145°C	9.71	2154	11.5	545	3.4
Soot steam 3.6 MPa, 420°C	0.22	589	3.2	115	0.7
Total:	15.21	14188	76.0	6297	38.9
Loss	04485		24.09889	61.1	
Unutilized outflow	9.9	2743	14.7	660	4.1
Efficiency			71.8		36.3
Ditto excluding the green liquor	70.5		27.3		

Steam plant	Weight:	Energy		Exergy	
	tonnes/tp	MJ/tp	%	MJ/tp	%
Inflow:					
Bark 25°C	0.44	4407	33.7	4275	36.8
Bottom blow 255°C	0.34	338	2.6	93	0.8
Water 108°C	3.75	1307	10.0	172	1.5
Fuel oil	0.16	7059	53.9	6843	59.0
Air 25°C	4.48	0		0	
Water 1°C	2.26	-228	-1.7	20	0.2
Electricity	-	203	1.6	203	1.7
Total:	11.43	13086	100	11606	100
Outflow:					
Steam 3.6 MPa, 404°C	2.79	8709	66.6	3360	29.0
Water 110°C	2.97	972	7.4	117	1.0
Exhaust gas 165°C-170°C	5.10	2134	16.3	513	4.4
Wastewater 25°C	0.57	0		0	
Total:	11.43	11815	90.3	3990	34.4
Losses	01271		9.77616	65.6	
Unutilized outflow	5.67	2134	16.3	513	4.4
Efficiency			88.4		31.3

Turbine plant	Weight:	Energy		Exergy	
	tonnes/tp	MJ/tp	%	MJ/tp	%
Inflow:					
Steam 3.6 MPa, 411°C	5.20	16329	98.9	6316	99.6
Water 108°C	0.53	185	1.1	25	0.4
Total:	5.73	16514	100	6341	100
Outflow:					
Steam 1.3 MPa, 205°C	0.79	2138	12.9	688	10.9
Steam 1.0 MPa, 200°C	2.55	6942	42.0	2159	34.0
Steam 0.5 MPa, 175°C	2.39	6454	39.1	1775	28.0
Electricity	-	977	5.9	977	15.4
Total:	5.73	16511	100	5599	88.3
Losses	0 3	0	742	11.7	
Unutilized outflow	0	0		0	
Efficiency			100.0		88.3

Lime sludge reburning kiln and causticizing department	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Green liquor 90°C	2.43	3487	72.5	2588	67.7
Water 50°C	0.99	104	2.2	4	0.1
Fuel oil	0.3	1200	25.0	1163	30.4
Air 25°C	0.16	0		0	
Water 1°C	0.48	-48	-1.0	4	0.1
Electricity	-	65	1.4	65	1.7
Total:	4.09	4808	100	3825	100
Outflow:					
White liquor 85°C	1.97	3946	82.1	2875	75.2
Weak liquor 55°C	1.93	730	15.2	439	11.5
Exhaust gas 250°C	0.19	116	2.4	31	0.8
Total:	4.09	4792	99.7	3345	87.5
Losses	016	0.3	479	12.5	
Unutilized outflow	0.19	116	2.4	31	0.8
Efficiency			99.7		87.4

Paper mill	Weight: tonnes/tp	Energy MJ/tp	Energy %	Exergy MJ/tp	Exergy %
Inflow:					
Pulp 55°C	5.90	19576	62.3	18296	69.3
Steam 1.0 MPa, 200°C	2.55	6942	22.4	2159	8.2
Water 50°C	9.87	1033	3.3	42	0.2
Waste paper -16°C	0.27	4023	13.0	3911	14.8
Water 1°C	7.39	-744	-2.4	65	0.2
Air -16°C	43.52	-1711	-5.5	130	0.5
Electricity	-	1809	5.8	1809	6.8
Total:	69.50	30928	100	26412	100
Outflow:					
Condensate 118°C	2.12	829	2.7	108	0.4
Air 30°C	43.52	213	0.7	2	0.0
Paper 65°C	1	23011	74.4	22177	84.0
Damp air 55°C	2.07	4680	15.1	479	1.8
Water 55°C	13.01	1635	5.3	77	0.3
Wastewater 25°C	7.78	0		0	
Total:	69.50	30368	98.2	22843	86.5
Losses	0560	1.83569		13.5	
Unutilized outflow	22.86	6315	20.4	556	2.1
Efficiency			99.7		86.2

Appendix 2. Material, energy och exergy flows in a steel mill

Electric furnaces	Weight:	Energy		Exergy	
		Total (thermal)		Total (thermal)	
	kg/tr	MJ/tr	%	MJ/tr	%
Inflow:					
Scrap iron	1075	7651	65.2	6936	63.9
Electricity	-	2363	20.1	2363	21.8
Cast-iron	96	838	7.1	774	7.1
Pig-iron	16	138	1.2	128	1.2
Sinter	24	34	0.3	26	0.2
Alloys	22	310	2.6	288	2.7
Burnt lime	57	181	1.5	119	1.1
Limestone	1	0		0	
Magnesite	9	9	0.1	3	0.0
Bricks	11	-	-		
Electrodes	6	210	1.8	219	2.0
Water 25°C	17000	0		0	
Total:	18317	11734	100	10856	100
Outflow:					
Steel 1650°C	1141	10272(1662)	87.5	8997(1189)	82.9
Slag 1650°C	96	418 (170)	3.6	292 (113)	2.7
Water 30°C	17000	356 (356)	3.0	3 (3)	0.0
Loss by burning 1650°C	68	157 (73)	1.3	127 (51)	1.2
Exhaust gas 1000°C[a]	28	284 (27)	2.4	265 (14)	2.4
Total:	18333	11487(2288)	97.9	9684(1379)	89.2
Loss[b]	16	247	2.1	1172	10.8
Unutilized outflow		1215	10.4	687	6.3
Efficiency			97.7		88.5

[a] The temperature of the exhaust gas from the melt varies between 500 and 1500°C. As the carbon monoxide is combusted, it generates heat which is given off outdoors prior to the stack cleaner.

[b] The air flow into the process cannot be calculated. However, this does not effect the energy and exergy flows.

Continuous casting	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Steel 1650°C	1141	10272	(1662)	98.5	8997	(1189)	98.3
Water 25°C	7020	0			0		
Electricity	-	160		1.5	160		1.7
Total: 8161	10432	(1662)	100	9157	(1189)	100	
Outflow:							
Steel 850°C	1089	8826	(608)	84.6	7794	(340)	85.1
Scrap 850°C	48	389	(28)	3.7	344	(15)	3.8
Embers 4	-			-			
Water 55°C	4860	610	(610)	5.8	29	(29)	0.3
Water 35°C	2160	90	(90)	0.9	1	(1)	0.0
Total: 8161	9915	(1336)		95.08168	(385)	89.2	
Loss 0	517			5.0989		10.8	
Unutilized outflow		517		6.7	30		0.3
Efficiency				94.5			89.1

Pusher type furnace (mill 5)	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Steel 75°C[a]	657	4973	(15)	77.0	4498	(1)	78.0
Fuel oil	29	1247		19.3	1198		20.8
Air 330°C	752	235	(235)	3.6	74	(74)	1.3
Total:	1438	6455	(250)	100	5770	(75)	100
Outflow:							
Steel 1150°C	657	5460	(502)	84.6	4805	(308)	83.3
Exhaust gas 850°C[a]	781	820	(820)	12.7	409	(401)	7.1
Total:	1438	6280	(1322)	97.3	5214	(709)	90.4
Loss	0	175		2.7	556		9.6
Unutilized outflow		0			0		
Efficiency				97.3			90.4
Efficiency[b]				88.2			55.7
Efficiency[c]				73.6			35.2

[a] Estimated value

[b] Total heating

[c] Heating of the steel

Recuperative heat exchanger (mill 5)	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Exhaust gas 850°C[a]	781	820	(820)	100	409	(401)	100
Air 25°C	752	0			0		
Total:	1533	820	(820)	100	409	(401)	100
Outflow:							
Exhaust gas 500°C	781	500	(500)	61.0	191	(183)	46.7
Air 330°C	752	235	(235)	28.7	74	(74)	18.1
Total:	1533	735	(735)	89.6	265	(257)	64.8
Loss	0	85		10.4	144		35.2
Unutilized outflow		500		61.0	191		46.7
Efficiency				73.4			33.9

[a]Estimated value

Rolling-mill (mill 5)	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Steel 1150°C	657	5460	(502)	96.2	4805	(308)	95.5
Electricity	-	217		3.8	217		4.3
Total:	657	5677	(502)	100	5022	(308)	100
Outflow:							
Steel 850°C	614	4974	(340)	87.6	4393	(191)	87.5
Scrap 850°C	23	186	(13)	3.3	165	(7)	3.3
Embers 850°C	20	36	(8)	0.6	28	(6)	0.6
Total:	657	5196	(361)	91.5	4586	(204)	91.3
Loss	0	481		8.5	436		18.7
Unutilized outflow		13		0.2	10		0.2
Efficiency				91.5			91.3

Walking beam furnace (mill 6)	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Steel 75°C[a]	432	3270	(10)	78.9	2958	(1)	79.5
Fuel oil	17	744		18.0	721		19.4
Air 350°C	384	128	(128)	3.1	42	(42)	1.1
Total:	833	4142	(138)	100	5770	(43)	100
Outflow:							
Steel 1150°C	432	3590	(330)	86.7	3159	(203)	84.9
Exhaust gas 850°C	401	421	(421)	10.2	210	(206)	5.6
Total:	833	4011	(751)	96.8	3369	(409)	90.5
Loss	0	131		3.2	352		9.5
Unutilized outflow		0			0		
Efficiency				96.8			90.5
Efficiency[a]				85.0			53.5
Efficiency[b]				71.0			36.5

[a] Total heating
[b] Heating of steel

Recuperative heat exchanger (mill 6)	Weight:	Energy			Exergy		
		Total	(thermal)		Total	(thermal)	
	kg/tr	MJ/tr		%	MJ/tr		%
Inflow:							
Exhaust gas 850°C	401	421	(421)	100	210	(206)	100
Air 25°C	384	0			0		
Total:	785	421	(421)	100	210	(206)	100
Outflow:							
Exhaust gas 350°C	401	189	(189)	44.9	59	(55)	28.1
Air 350°C	384	128	(128)	30.4	42	(42)	20.0
Total:	785	317	(317)	75.3	101	(97)	48.1
Loss	0	104		24.7	109		51.9
Unutilized outflow		75		17.8	23		11.0
Efficiency				55.2			27.8

Flue gas boiler (mill 6)	Weight: kg/tr	Energy Total MJ/tr	Energy (thermal)	Energy %	Exergy Total MJ/tr	Exergy (thermal)	Exergy %
Inflow:							
Exhaust gas 350°C[a]	241	114	(114)	100	36	(33)	100
Air 25°C	-	0			0		
Total:	241	114	(114)	100	36	(33)	100
Outflow:							
Steam[a]	-	30	(30)	26.3	10	(10)	27.8
Exhaust gas 200°C	241	74	(74)	64.9	18	(15)	50.0
Total:	241	104	(104)	91.2	28	(25)	77.8
Loss	0	10		8.8	8		22.2
Unutilized outflow		74		64.9	18		50.0
Efficiency				75.0[a]			55.6

[a]Estimated value.

Rolling-mill (mill 6)	Weight: kg/tr	Energy Total MJ/tr	Energy (thermal)	Energy %	Exergy Total MJ/tr	Exergy (thermal)	Exergy %
Inflow:							
Steel 1150°C	432	3590	(330)	93.1	3159	(203)	92.2
Electricity	-	266		6.9	266		7.8
Total:	432	3856	(330)	100	3425	(203)	100
Outflow:							
Steel 850°C	386	3126	(218)	81.1	2762	(120)	80.6
Scrap 850°C	36	292	(20)	7.6	258	(11)	7.5
Embers 850°C	10	18	(4)	0.5	14	(3)	0.4
Total:	432	3436	(242)	89.1	3034	(60)	88.5
Loss	0	420		10.9	391		11.5
Unutilized outflow		7		0.2	6		0.2
Efficiency				89.1			88.4

Appendix 3. Computer program in BASIC for calculating the exergy, energy, enthalpy and entropy of steam

```
10 REM "STEAM" 830210
20 REM ref. J.H. Keenan et. al. "Steam Tables" and
30 REM W.C. Reynolds "Thermodynamic Properties in SI"
40 REM
50 REM TDS 500, CP/M
60 REM*************************************************
70 REM
80 REM Steam Properties in SI Units
90 REM
100 REM***********************************************
110 REM February 1983
120 REM Göran Wall
130 REM***********************************************
140 REM Pressure range: 001 to 100 MPa
150 REM
160 REM Temperature range: 0 to 1300 C
170 REM
180 REM Slow but steam table accurracy
190 REM
200 REM***********************************************
210 REM
220 GOSUB 1000: REM Initiate
230 GOSUB 2000: REM Input
240 GOSUB 3000: REM Calculate
245 GOSUB 8000: REM Calculate U, H, S and E
246 TH=T: PH=P: RH=RO : UH=U: HH=H: SH=S : EH=E
250 GOSUB 9000: REM Print
255 PRINT
260 INPUT " Do you want another run? yes=1/no=0 ",PL
270 IF PL=1 THEN 230
280 PRINT
290 PRINT "If you would like to calculate the reversible change to a
   lower pressure answer this question, if not, just print 0"
300 PRINT
310 INPUT "Low pressure in MPa: " ,PL
320 IF PL=0 THEN 900
330 GOSUB 4440: REM Calculate T, U, H, S, and E at PL and SR
340 GOSUB 4190: REM Calculate T, U, H, S, and E at PL and SR
350 TL=T: PL=P: RL=RO: UL=U:, HL=H: SL=S: EL=E
360 GOSUB 9000: REM Print
370 GOSUB 9150: REM Print the difference
900 END
1000 REM Initiate
1010 RETURN
2000 REM Input
2010 INPUT "Pressure in MPa: ",P
2020 INPUT "Temperature in °C: ",TC
2025 INPUT "Approximate inaccuracy in percent, 0 will give steam table
   accuracy: ",IC
2026 IC=IC/100+.000001
2030 T=TC+273.15
2040 RETURN
3000 REM Calculation of RO, Q, QR, F, and FT at T and P high
```

```
4000 REM Calculation of RO (the density) from given values of pressure
   and temperature by iteration
4010 REM
4020 TA=1000/T
4030 N=2
4040 X1=0: REM starting value
4050 F1=P: REM since RO=0
4060 RO=P/.46151/T
4070 GOSUB 5000: REM calculate Q, QT and QR
4080 F0=F1
4090 F1=P-RO*.46151*T*(1+RO*(Q+RO*QR))
4100 IF FO*F1< 0 THEN N=5
4110 X0=X1
4120 X1=RO
4130 RO=X1+SGN(FO*F1)*(X1-X0)*N
4140 IF ABS(X0-X1)> IC*ABS(X1) THEN 4070
4150 GOSUB 6000: REM Calculate F and FT
4160 RETURN
4170 REM
4180REM
4190 REM Calculation of T from given values of pressure and entropy by
   iteration
4200 REM
4210 N=2: REM First stepping in 10ths of degrees
4220 P=PL
4230 SR=S: REM Save the earlier value of the entropy
4240 T=TS-!==: REM Starting value 100 degrees under saturation curve
4250 GOSUB 4000: REM Calculate RO, Q, QT and QR at T and P
4260 GOSUB 6000: REM Calculate F and FT
4270 GOSUB 8000: REM Calculate S at T and P
4280 F1=SR-S
4290 X1=T
4300 T=T+10*K
4310 GOSUB 4000
4320 GOSUB 6000
4330 GOSUB 8000
4340 F0=F1
4350 F1=SR-S
4360 IF FO*F1<0 THEN N=.5
4370 X0=X1
4380 X1=T
4390 T=X1+SGN(F0*F1)*X1-X0)*N
4400 IF ABS(T-X1) > IC*ABS(T) THEN 4310
4410 RETURN
4420 REM
4430 REM
4440 REM Calculation of saturation temperature from given value of
   pressure by iteration
4450 REM
4460 N=2: REM Stepping in 10ths of degrees
4470 T=273: REM Starting value
4480 GOSUB 7000: REM Calculate the saturation pressure at T
4490 F1=PL-PS: REM Starting value
4500 X1=T
4510 T=T+10*N
4520 GOSUB 7000
4530 F0=F1
4540 F1=PL-PS
```

```
4550 IF F0*F1< 0 THEN N=.5
4560 X0=X1
4570 X1=T
4580 T=X1+SGN (F0*F1)*(X1-X0)*N
4581 PRINTT
4590 IF ABS 8T-X1) >IC*ABS(T) THEN 4520
4600 TS=T
4610 PRINT "Saturation temperature: TS = " , INT(TS-273.15)*100)/100,"
   C"
4620 RETURN
4630 REM
4640 REM
5000 X=RO-1: REM X=RO-R(AJ) where R(AJ) =1 for J >1
5010 Y=RO-.634: REM Y=RO-R (AJ) where R(AJ)=.634 for J=1
5020 Z=EXP(-4.8*RO): REM Z=EXP(-E*RO)
5030 T1=TA-1.544912#: REM T1=TA-TA(AJ) where TA(AJ)=TCRIT=1.544912 for
   J=1
5040 B=TA-2.5: REM B=TA-TA(AJ) where TA(AJ)=2.5 for J >1
5050 REM
5060 REM
5070 REM Calculation of Q (RO,TA) and QT (RO,TA)
5080 REM
5090 A1=29.492937#+(-132.13917#+(274.64632#+(-360.93826#+(342.18431#+(-
   244.50042#+(155.18535#+5.9728487#*Y)*Y)*Y)*Y)*Y)*Y)*Y-
   Z*(410.30848#+416.0586#*RO)
5100 A2=-5.198586#+(7.7779182#+(-33.301902#+(-16.254622#+(-
   177.31074#+(127.48742#+(137.46153#+155.97836#*X)*X)*X)*X)*X)*X)*X+Z*
   (337.3118#-209.88866#*RO)
5110 A3=6.8335354#+(-26.149751#+(65.326396#-26.181978#*X)*X)*X-
   Z*(137.46618#+733.96848#*RO)
5120 A4=-.1564104#+(-.72546108#+(-
   9.2734289#+4.312584#*X)*X)*X+Z*(6.7874983#+10.401717#*RO)
5130 A5=-6.3972405#+(26.409282#+(-
   47.740374#+56.32313#*X)*X)*X+Z*(136.87317#+645.8188#*RO)
5140 A6=-3.9661401#+(15.453061#+(-
   29.14247#+29.568796#*X)*X)*X+Z*(79.84797#+399.1757#*RO)
5150 A7=-.69048554#+(2.7407416#+(-
   5.102807#+3.9636085#*X)*X)*X+Z*(13.041253#+71.531353#*RO)
5160 A=A2+B*(A3+B*(A4+B*(A5+B*(A6+B*A7))))
5170 Q=A1+T1*A
5180 QT=A+T1*(A3+B*(2*A4+B*(3*A5+B*(4*A6+B*5*7))))
5190 REM
5200 REM
5210 REM Calculation of QR (RO,TA)
5220 REM
5230 R1=-132.13917#+(549.29264#+(-1082.81484#+(1368.73724#+(-
   1222.5021#+(931.1121#+41.8099409#*Y)*Y)*Y)*Y)*Y)*Y-Z*(416.0586#-
   4.8*(410.39848#+416.0586#*RO))
5240 R2=7.7779182#+(-66.603804#+(-48.763866#+(-
   709.24296#+(637.4371#+(824.76918#+10991.84842#*X)*X)*X)*X)*X)*X+Z*(-
   209.88866#-4.8*(337.3118#-209.88866#*RO))
5250 R3=-26.149751#+(130.652792#-78.545934#*X)*X+Z*(-
   733.96848#+4.8*(137.46618#+733.96848#*RO))
5260 R4=-.72546108#+(-18.5468578#+12.937752#*X)*X+Z*(10.401717#-
   4.8*(6.7874983#+10.401717#*RO))
5270 R5=26.409282#+(-95.480748#+168.96939#*X)*X+Z*(645.8188#-
   4.8*(136.87317#+645.8188#*RO))
```

```
5280 R6=15.453061#+(-58.28494#+88.706388#*X)*X+Z*(399.1757#-
   4.8*(79.84797#+399.1757#*RO))
5290 R7=2.7407416#+(-10.205614#+11.8908255#*X)*X+Z*(71.531353#-
   4.8*(13.041253#+71.531353#*RO))
5300 QR=R1+T1*(R2+B*(R3+B*(R4+B*(R5+B*(R6+B*R7)))))
5310 RETURN
5320 REM
5330 REM
6000 REM Calculation of F(TA) and FT(TA) where F=fi0
6010 REM
6020 F=1857.065#+((((-20.5516+4.85233/TA)/TA+36.6649)/TA-
   419.465)/TA+3229.12)/TA+(6.90775528#-LOG(TA))*(46-1011.249#/TA)
6030 FT=(-1*((((-82.2064+24.26165#/TA)/TA+109.9947#)/TA-
   838.93)/TA+3229.12)/TA-(46-1011.249#/TA)+(6.90775528#-
   LOG(TA))*(1011.249#/TA))/TA
6040 RETURN
6050 REM
6060 REM
7000 REM Calculation of saturation pressure from given value of
   temperature
7010 REM
7020 AS=.01*(T-338.15)
7030 PS=22.089*EXP((1-T/647.286)*(-7.419242#+AS*(.29721+AS*(-
   .1155286#+AS*(.008685635#+AS*(.001094098#+AS*(-4.39993E-
   03+AS*(.002520658#-AS*.0005218684#))))))))
7040 RETURN
7050 REM
7060 REM
8000 REM Calculation of U, H, S and E
8010 REM
8020 U=RO*461.51*QT+TA*FT+F
8030 H=U+P/RO
8040 S=-.46151*(LOG(RO)+RO*Q-RO*TA*QT)+TA*TA*FT/1000
8050 E=H-298.15*S
8060 RETURN
8070 REM
8080 REM
9000 PRINT
9010 PRINT "Temperature: ", INT( (T-273.15)*100)/100, "C"
9020 PRINT "Pressure: ", INT(P*1000) /1000, " MPa"
9030 PRINT "Density: ", INT(1E+06*RO) /1000," kg/m3
9040 PRINT "Specific volume: "INT(1000/RO) /1000, " *1000m 3/kg"
9050 PRINT
9060 PRINT "Energy : U= ", INT(100*U)/100," kJ/kg
9070 PRINT "Enthalpy: H= ", INT(100*H)/100," kJ/kg
9080 PRINT "Entropy: S= ", INT(100000!*S) /100000!," kJ/kg K"
9090 PRINT "Exergy: E= ", INT(100*E) /100," kJ/kg"
9100 PRINT
9110 PRINT "Remember the innaccuracy in the input values of ",
   INT(IC*1000) /10," %"
9120 PRINT
9130 PRINT
9140 RETURN
9150 PRINT
9160 PRINT"The difference between the two states is"
9170 PRINT
9180 PRINT "Temperature: ", INT( (TH-TL)*100) /100," C"
9190 PRINT "Pressure: ", INT( (PH-PL)*1000) /1000," MPa"
```

```
9200 PRINT "Energy: ", INT( (UH-UL)*100) /100," kJ/kg
9210 PRINT "Enthalpy: ", INT( (HH-HL)*100) /100," kJ/kg
9220 PRINT "Entropy: ", INT( (SH-SL)*1E+06," kJ/kg K"
9230 PRINT "Exergy: ", INT ( (EH-EL)*100) /100," kJ/kg
9240 PRINT
9250 PRINT "Remember the inaccuracy in the input values of ",
   INT(IC*1000) /10," %"
9260 RETURN
```

Appendix 4. Computer program in BASIC for calculating the thermal and chemical energies and exergies of some substances

```
1 REM "EXERGY"
2 REM 830407-
3 REM References: CRC "Rubber book" 63rd ed pp. D-45 etc.
4 REM
5 REM
6 REM Thermal and chemical exergies of some substances
7 REM
8 REM April 1983
9 REM Göran Wall
10 REM
11 REM This program calculates the thermal and chemical exergies of some
   elements and ideal or nonideal mixtures of theme at constant
   pressure
12 REM
20 GOSUB 11000: REM initialize
21 GOSUB 11500: REM input
22 GOSUB 11900: REM calculate
23 GOSUB 12490: REM convert
24 GOSUB 12820: REM calculate the chemical exergy
26 REM GOSUB 15000: rem print
27 GOSUB 13370: REM mass flow
40 PRINT
50 INPUT "Another run? Yes=1/No=0 ",Q
60 PRINT
61 FOR I=1 TO 26 : FOR K=0 TO 3:C(I,K)=100*C(I,K): NEXT K: NEXT I
70 IF Q=0 THEN GOTO 96
71 GOSUB 11580: REM input
72 GOTO 22
96 END
97 REM
100 REM Hydrogen, £1,0
101 A=6.62:B=,81: GOSUB 12340
102 HT(1,0)=H:ST(1,0)=S
103 RETURN
104 REM
105 REM H20, £1,1
106 IF T <373.16 THEN GOTO 109
107 HT=9.77:ST=26.18
108 A=7.17:B=2.56:D=-.08:T1=373.16: GOSUB 12340
109 A=18.03: GOSUB 12340
110 HT(1,1)=HT:ST(1,1)=ST
111 RETURN
112 REM
200 REM Helium, £2, 0
201 A=4.96793: GOSUB 12340: REM Ideal monoatomic gas
202 HT(2,0)=HT:ST(2,0)=ST
203 RETURN
204 REM
600 REM Carbon £6,0
601 A=4.1:B=1.02:D=-2.1: GOSUB 12340
602 HT(6,0)=H:ST(6,0)=S
603 RETURN
604 REM
```

```
605 REM CO, £6,1
606 A=6.6:B=1.2: GOSUB 12340
607 HT(6,1)=HT:ST(6,1)=ST
608 RETURN
609 REM
610 REM CO2, £6,2
611 A=7.7:B=5.3:C=-.83: GOSUB 12340
612 HT(6,2)=HT:ST(6,2)=ST
613 RETURN
614 REM
615 REM CH4, £6,3 to 1500 K ref. Zemansky
616 A=3.38:B=17.905:C=-4.188: GOSUB 12340
617 HT(6,3)=HT:ST(6,3)=ST
618 RETURN
619 REM
700 REM Nitrogen, £7
701 A=6.76:B=.606:C=.13: GOSUB 12340
702 HT(7,0)=H:ST(7,0)=S
703 RETURN
704 REM
705 REM N20, £7,1
706 A=10.92:B=2.06:D=-2.04: GOSUB 12340
707 HT(7,1)=HT:ST (7,1)=ST
708 RETURN
709 REM
800 REM Oxygen, £8,0
801 A=8.27:B.258:D=-1.877: GOSUB 12340
802 HT(8,0)=H:ST(8,0)=ST
803 RETURN
804 REM
1000 REM Neon, £10,0
1001 A=4.96793: GOSUB 12340
1002 HT(10,0)=HT:ST(10,0)=ST
1003 RETURN
1004 REM
1100 REM Sodium, Na 11,0
1101 IF T < 371 THEN GOTO 1107
1102 HT=.63:ST=1.7
1103 IF T<1187 THEN GOTO 1106
1104 HT=HT+23.4:ST=ST+20.1
1105 A=4.97:T1=1187: GOSUB 12340
1106 A=8.954:B=-4.577:C=2.54:T1=371: GOSUB 12340
1107 A=5.657:B=3.252:C=.5785: GOSUB 12340
1108 HT(11,0)=HT:ST(11,0)=ST
1109 RETURN
1110 REM
1111 REM Na2CO3 11,1 (Simple model)
1112 GOSUB 1100
1113 GOSUB 600
1114 GOSUB 800
1115 HT(11,1)=HT(11,0)/3+HT(6,0)/6+HT(8,0)/4
1116 ST(11,1)=ST(11,0)/3+ST(6,0)/6+ST(8,0)/4
1117 RETURN
1118 REM
1119 REM NaOH 11,2 (Simple model)
1120 GOSUB 1100
1121 GOSUB 800
1122 GOSUB 100
```

```
1123 HT(11,2)=HT(11,0)/3+HT(8,0)/6+HT(1,0)/6
1124 ST(11,2)=ST(11,0)/3+ST(8,0)/6+ST(1,0)/6
1125 RETURN
1126 REM
1127 REM Na2S 11,3 (Simple model)
1128 GOSUB 1100
1129 GOSUB 1600
1130 HT(11,3)=HT(11,0)*2/3+HT(16,0)/3
1131ST(11,3)=ST(11,0)*2/3+ST(16,0)/3
1132 RETURN
1133 REM
1300 REM Aluminium, #13,0
1301 IF T<931.7 THEN GOTO 1310
1302 HT=2.57:ST=2.76
1303 IF T<2600 THEN GOTO 1309
1304 IF INT(T)=2600 THEN GOTO 1307
1305 PRINT "The temperature must not exceed 2600 K for Aluminum"
1306 RETURN
1307 PRINT "Aluminum boils"
1308 HT=HT+67.9:ST=ST+26
1309 A=7:T1=931.7: GOSUB 12340
1310 A=4.94:B=2.96: GOSUB 12340
1311 HT(13,0)=HT:ST(13,0)=ST
1312 RETURN
1313 REM
1314 REM Al2O3, #13,1
1315 IF T<2300 THEN GOTO 1319
1316 PRINT "Al2O3 decays"
1317 HT=26:ST=11
1318 A=33:T1=230: GOSUB 12340
1319 A=26.12:B=4.388:D=-7.269: GOSUB 12340
1320 HT(13,1)=HT:ST(13,1)=ST
1321 RETURN
1322 REM
1400 REM Silicon, Si 14,0
1401 IF T < 1683 THEN GOTO 1410
1402 HT=11.1:ST=6.6
1403 IF T<2750 THEN GOTO 1409
1404 IF INT(T)=2750 THEN GOTO 1407
1405 PRINT "The temperature must not exceed 2750 K for Silicon"
1406 RETURN
1407 PRINT "Silicon boils"
1408 HT=HT+71:ST=ST+26
1409 A=7.4:T1=1683: GOSUB 12340
1410 A=5.7:B=1.02:D=-1.06: GOSUB 12340
1411 HT(14,0)=HT:ST(14,0)=ST
1412 RETURN
1413 REM
1414 REM SiO #14,1
1415 IF T<2550 THEN GOTO 1421
1416 IF INT(T)=2550 THEN GOTO 1419
1417 PRINT "SiO decays over 2550 K"
1418 GOTO 1423
1419 PRINT "SiO decays"
1420 HT=12:ST=4.7
1421 A=7.3:B=2.4: GOSUB 12340
1422 HT(14,1)=HT:ST(14,1)=ST
1423 RETURN
```

```
1424 REM
1425 REM SiO2, #14,2
1426 IF T<856 THEN GOTO 1435
1427 HT=.15:ST=.18
1428 IF T<1883 THEN GOTO 1434
1429 HT=HT+2.04:ST=ST+1.08
1430 IF T<2250 THE GOTO 1433
1431 PRINT "SiO decays over 2250 K"
1432 GOTO 1437
1433 A=20:T1=1883: GOSUB 12340
1434 A=14.41:B=1.94:T1=856: GOSUB 12340
1435 A=11.22:B=8.2:D=-2.7: GOSUB 12340
1436 HT(14,2)=HT:ST(14,2)=ST
1437 RETURN
1438 REM
1500 REM Phosphorus, #15,0
1501 IF T < 317.4 THEN GOTO 1507
1502 HT=.601:ST=1.89
1503 IF T<553 THEN GOTO 1506
1504 HT=HT+11.9:ST=ST+21.5
1505 A=19.5:B=-.4:C=1.3:T1=553: GOSUB 12340
1506 A=19.23:B=.51:C=-2.98:T1=317.4: GOSUB 12340
1507 A=13.62:B=28.72: GOSUB 12340
1508 HT(15,0)=HT:ST(15,0)=ST
1509 RETURN
1510 REM
1600 REM Sulphur, #16,0
1601 IF T < 368.6 THEN GOTO 1610
1602 HT=.088:ST=.24
1603 IF T<392 THEN GOTO 1609
1604 HT=HT+.293:ST=ST+.747
1605 IF T<717.76 THEN GOTO 1608
1606 HT=HT+2.5:ST=ST+3.5
1607 A=4.25:B=.15:D=-1:T1=717.76: GOSUB 12340
1608 A=5.4:B=5:T1=392: GOSUB 12340
1609 A=3.56:B=6.95:T1=368.6: GOSUB 12340
1610 A=3.58:B=6.24: GOSUB 12340
1611 HT(16,0)=HT:ST(16,0)=ST
1612 RETURN
1613 REM
1614 REM SO2, #16,1
1615 A=11.4:B=1.414:C=-2.045: GOSUB 12340
1616 HT(16,1)=HT:ST(16,1)=ST
1617 RETURN
1618 REM
1800 REM Argon, #18, 0
1801 A=4.96793: GOSUB 12340: REM Ideal monoatomic gas
1802 HT(18,0)=HT:ST(18,0)=ST
1803 RETURN
1804 REM
2000 REM Calcium, #20,0
2001 IF T < 723 THEN GOTO 2010
2002 HT=.24:ST=.33
2003 IF T<1123 THEN GOTO 2009
2004 HT=HT+2.2:ST=ST+1.96
2005 IF T<1755 THEN GOTO 2008
2006 HT=HT+38.6:ST=ST+22
2007 A=4.97:T1=1755: GOSUB 12340
```

```
2008 A=7.4:T1=1123: GOSUB 12340
2009 A=6.29:B=1.4:T1=723: GOSUB 12340
2010 A=5.24:B=3.5: GOSUB 12340
2011 HT(20,0)=HT:ST(20,0)=ST
2012 RETURN
2013 REM
2014 REM CaO, #20,1
2015 IF T<2860 THEN GOTO 2021
2016 IF INT(T)=2860 THEN GOTO 2019
2017 PRINT "CaO decays over 2860 K"
2018 GOTO 2023
2019 PRINT "CaO decays"
2020 HT=18:ST=6.3
2021 A=10:B=4.84:D=-1.08: GOSUB 12340
2022 HT(20,1)=HT:ST(20,1)=ST
2023 RETURN
2024 REM
2300 REM Vanadium, 23,0
2301 IF T < 2003 THEN GOTO 2308
2302 HT=4:ST=2
2303 IF T<3800 THEN GOTO 2307
2304 IF INT(T)=3800 THEN GOTO 2307
2305 PRINT "The temperature must not exceed 3800 K for Vanadium"
2306 RETURN
2307 A=8.6:T1=2003: GOSUB 12340
2308 A=5.57:B=.97: GOSUB 12340
2309 HT(23,0)=HT:ST(23,0)=ST
2310 RETURN
2311 REM
2400 REM Cromium, Na 24,0
2401 IF T < 2173 THEN GOTO 2407
2402 HT=3.5:ST=1.6
2403 IF T<2495 THEN GOTO 2406
2404 HT=HT+72.97:ST=ST+29.25
2405 A=4.97:T1=2495: GOSUB 12340
2406 A=9.4:T1=2173: GOSUB 12340
2407 A=5.35:B=2.36:C=-44: GOSUB 12340
2408 HT(24,0)=HT:ST(24,0)=ST
2409 RETURN
2410 REM
2500 REM Manganese, #25,0
2501 IF T < 1000 THEN GOTO 2516
2502 HT=.535:ST=.535
2503 IF T<1374 THEN GOTO 2515
2504 HT=HT+.545:ST=ST+.397
2505 IF T<1410 THEN GOTO 2514
2506 HT=HT+.43:ST=ST+.305
2507 IF T<1517 THEN GOTO 2513
2508 HT=HT+3.5:ST=ST+2.31
2509 IF T<2368 THEN GOTO 2512
2510 HT=HT+53.7:ST=ST+22.7
2511 A=6.26:T1=2368: GOSUB 12340
2512 A=11:T1=1517 GOSUB 12340
2513 A=11.3:T1=1410: GOSUB 12340
2514 A=10.7:T1=1374: GOSUB 12340
2515 A=8.33:B=.66:T1=1000: GOSUB 12340
2516 A=5.7:B=3.38:D=-.377: GOSUB 12340
2517 HT(25,0)=HT:ST(25,0)=ST
```

```
2518 RETURN
2519 REM
2520 REM MnO, #25,1
2521 IF T<2058 THEN GOTO 2525
2522 HT=13:ST=6.32
2523 PRINT "MnO decays 2058"
2524 A=13.5:T1=2058: GOSUB 12340
2525 A=11.11:B=1.94:D=-.88: GOSUB 12340
2526 HT(25,1)=HT:ST(25,1)=ST
2527 RETURN
2528 REM
2600 REM Iron, Fe #26,0
2601 IF T < 1033 THEN GOTO 2619
2602 HT=.41:ST=.397
2603 IF T<1180 THEN GOTO 2618
2604 HT=HT+.217:ST=ST+.184
2605 IF T<1673 THEN GOTO 2617
2606 HT=HT+.15:ST=ST+.084
2607 IF T<1808 THEN GOTO 2616
2608 HT=HT+3.86:ST=ST+2.14
2609 IF T<3008 THEN GOTO 2615
2610 IF INT(T)=3008 THEN GOTO 2613
2611 PRINT"The temperature must not exceed 3008 K for Iron"
2612 RETURN
2613 PRINT"Iron boils"
2614 HT=HT+84.62:ST=ST+28.1
2615 A=10:T1=1808: GOSUB 12340
2616 A=10.3:T1=1673 GOSUB 12340
2617 A=4.85:B=3:T1=1180: GOSUB 12340
2618 A=10.4:T1=1033: GOSUB 12340
2619 A=3.37:B=7.1:D=.43: GOSUB 12340
2620 HT(26,0)=HT:ST(26,0)=ST
2621 RETURN
2622 REM
2623 REM FeO 26,1
2624 IF T<1641 THEN GOTO 2633
2625 HT=7.5:ST=4.6
2626 IF T<2700 THEN GOTO 2632
2627 IF INT(T)=2700 THEN GOTO 2630
2628 PRINT "The temperature must not exceed 2700 K for FeO"
2629 RETURN
2630 PRINT "FeO boils"
2631 HT=HT+55:ST+20
2632 A=14.5:T1=1641: GOSUB 12340
2633 A=9.27:B=4.8: GOSUB 12340
2634 HT(26,1)=HT:ST(26,1)=ST
2635 RETURN
2636 REM
2637 REM Fe2O3 26,2
2638 IF T<950 THEN GOTO 2643
2639 HT=.16:ST=.17
2640 IF T<1050 THEN GOTO 2643
2641 PRINT"Fe2O3 decays"
2642 A=23.46:B=18.6:D=-3.55:T1=1050: GOSUB 12340
2643 A=48:T1=950: GOSUB 12340
2644 A=21.88:B=48.2: GOSUB 12340
2645 HT(26,2)=HT:ST(26,2)=ST
2646 RETURN
```

```
2647 REM
2648 REM Fe3O4 26,3
2649 IF T<900 THEN GOTO 2652
2650 PRINT " Fe3O4 decays"
2651 A=14.5:T1=900: GOSUB 12340
2652 A=12.38:B=1.62:D=-.38: GOSUB 12340
2653 HT (26,3)=HT:ST(26,3)=ST
2654 RETURN
2655 REM
11000 REM Initialize
11010 R=8314.34:REM J/Kmol K
11020 N=26:K=7:DIMHT(N,K):DIMST(N,K):DIMET(N,K):DIMC(N,K):D
IMM(N,K):DIMX(N,K):DIMEC(N,K):DIMCF(N,K):DIMCA(N,K):DIMHC(N,K)
11030 EC=1:HC=0
11040 REM
11050 REM Molweight (kg/kmol)
11060 M(1,0)=2*1.0079
11070 M(1,1)=18.0152
11080 M(2,0)=4.0026
11090 M(6,0)=12.011
11100 M(6,1)=28.0104
11110 M(6,2)=44.0098
11120 M(6,3)=16.0426
11130 M(7,0)=2*14.0067
11140 M(7,1)=72.0262
11150 M(8,0)=2*15.9994
11160 M(10,0)=20.179
11170 M(11,0)=22.9898
11180 M(11,1)=105.989
11190 M(11,2)=39.9972
11200 M(11,3)=78.0436
11210 M(13,0)=26.9815
11220 M(13,1)=101.96128#
11230 M(14,0)=28.0855
11240 M(14,1)=44.0849
11250 M(14,2)=60.0843
11260 M(15,0)=4*30.9738
11270 M(16,0)=32.06
11280 M(16,1)=64.0588
11290 M(18,0)=39.948
11300 M(20,0)=40.08
11310 M(20,1)=56.0794
11320 M(20,2)=100.089
11330 M23,0)=50.9415
11340 M(24,0)=51.996
11350 M(25,0)=54.938
11360 M(25,1)=70.9374
11370 M(26,0)=55.847
11380 M(26,1)=71.8464
11390 M(26,2)=159.692
11400 M(26,3)=231.539
11410 RETURN
11420 REM
11430 REM Initialize H, S, T1 and T2
11440 HT=0
11450 ST=0
11460 T1=T0
11470 T2=T
```

```
11480 RETURN
11490 REM
11500 REM Input
11510 C=0
11520 INPUT"Element ? ?, Concentration in weight percent (-,-,0=no
   more)", I,K,C(I,K)
11530 C=C+C(I,K)
11540 IF C(I,K)=0 THEN GOTO 11580
11550 IF I=0 THEN GOTO 11890
11560 IF C=100 THEN GOTO 11580
11570 GOTO 11520
11580 PRINT
11590 CP=100
11600 FOR I=1 TO N: FOR K=0 TO 3
11610 IF C(I,K)=0 THEN GOTO 11640
11620 PRINT "C(",I,",",K,")=",C(I,K)," %"
11630 CP=CP-C(I,K)
11640 NEXT K: NEXT I
11650 I=0:K=0
11660 IF ABS(CP)<.01 THEN CP=0
11670 PRINT: IF CP<0 THEN GOSUB 11820: GOTO 11580
11680 PRINT"Unknown part: ",CP," %"
11690 INPUT"OK? yes=1/no=0 ",Q
11700 IF Q=0 THEN GOTO 11520
11710 FOR I=1 TO N: FOR K=0 TO 3
11720 C(I,K)=C(I,K) /100: REM Convertion to weight fraction
11730 NEXT K:NEXT I
11740 I=0:K=0:C=0
11750 CF=CP /100:REM Convertion to fraction
11760 PRINT
11770 PRINT"Reference temperature 25˚C = 298.15 Kelvin": T0=298.15
11780 PRINT
11790 INPUT "Actual temperature (Celsius): T=",T:T=T+273.15
11800 RETURN
11810 REM
11820 REM Normalization if sum C(I,K)>100
11830 FOR I=1 TO N: FOR K=0 TO 3
11840 C(I,K)=C(I,K) / (1-CP/100)
11850 NEXTK:NEXTI
11860 I=0:K=0:CP=0
11870 RETURN
11880 REM
11890 REM Special compositions
11900 REM Calculation of HT(I,K) and ST(I,K)
11910 A=0:B=0:C=0:D=0
11920 FOR I=1 TO N:FOR K=0 TO 3:REM Calculate HT(I,K) and ST(I,K),
   kcal/mol and cal/mol
11930 IF C(I,K)=0 THEN GOTO 12300
11940 GOSUB 11430
11950 IK=I+.1*K
11960 IF IK=1! THEN GOSUB 100
11970 IF IK=1.1 THEN GOSUB 105
11980 IF IK=2! THEN GOSUB 200
11990 IF IK=6! THEN GOSUB 600
12000 IF IK=6.1 THEN GOSUB 605
12010 IF IK=6.2 THEN GOSUB 610
12020 IF IK=6.3 THEN GOSUB 615
12030 IF IK=7! THEN GOSUB 700
```

```
12040 IF IK=7.1 THEN GOSUB 705
12050 IF IK=8! THEN GOSUB 800
12060 IF IK=10! THEN GOSUB 1000
12070 IF IK=11! THEN GOSUB 1100
12080 IF IK=11.1 THEN GOSUB 1111
12090 IF IK=11.2 THEN GOSUB 1119
12100 IF IK=11.3 THEN GOSUB 1127
12110 IF IK=13! THEN GOSUB 1300
12120 IF IK=13.1 THEN GOSUB 1314
12130 IF IK=14! THEN GOSUB 1400
12140 IF IK=14.1THEN GOSUB1414
12150 IF IK=14.2 THEN GOSUB 1425
12160 IF IK=15! THEN GOSUB 1500
12170 IF IK=16! THEN GOSUB 1600
12180 IF IK=16.1 THEN GOSUB 1614
12190 IF IK=18! THEN GOSUB 1800
12180 IF IK=11.1 THEN GOSUB 1614
12190 IF IK=11.2 THEN GOSUB 1800
12200 IF IK=20! THEN GOSUB 2000
12210 IF IK=20.1 THEN GOSUB 2014
12220 IF IK=23 THEN GOSUB 2300
12230 IF IK=24! THEN GOSUB 2400
12240 IF IK=25 THEN GOSUB 2500
12250 IF IK=25.1 THEN GOSUB 2520
12260 IF IK=26! THEN GOSUB 2600
12270 IF IK=26.1 THEN GOSUB 2623
12280 IF IK=26.2 THEN GOSUB 2637
12290 IF IK=26.3 THEN GOSUB 2648
12300 NEXT K: NEXT I
12310 I=0:K=0:IK=0
12320 RETURN
12330 REM
12340 REM Calculation of H and S at T (Kelvin)
12350 X=T2/T1
12360 H1=A*(X-1)
12370 H2=B*1E-03/2*(X^2-1)
12380 H3=C*-1E-06/3*(X^3-1)
12390 H4=D*100000! /T1*(1/X-1)
12400 H=T1*(H1+T1*(H2+T1*H3) )-H4
12410 H=H/1000: REM Mcal/kmol
12420 HT=HT+H
12430 S=A*LOG(X)+T1*(B*1E-03*(X-1)+T1*C*1E-06/2*(X*X-1) )-D*100000!
   /2/T1/T1*(1/X/X-1)
12440 ST=ST+S: REM kcal/kmol
12450 A=0:B=0:C=0:D=0
12460 T2=T1:T1=T0
12470 RETURN
12480 REM
12490 REM Calculation of thermal structural enthalpy, entropy and exergy
12500 REM Also conversion from weight fraction to mole fraction
12510 X=0
12520 FOR I=1 TO N: FOR K=0 TO 3
12530 IF C(I,K)=0 THEN GOTO 12550
12540 X=X+C(I,K)/M(I,K): REM Total number of kmol/kg known part of the
   mixture
12550 NEXT K: NEXT I
12560 X=X/(1-CF): REM Correction due to the unknown part assuming equal
   molar density
```

```
12570 I=0
12580 HM=0:SM=0:SS=0
12590 SX=0
12600 FOR I=1 TO N: FOR K=0 TO 3
12610 IF C(I,K)=0 THEN GOTO 12670
12620 X(I,K)=C(I,K)/M(I,K)/X: REM mole fraction
12630 IF X(I,K)=0 THEN GOTO 12670
12640 HM=HM+X(I,K)*HT(I,K)*4.184: REM mole fraction
12650 SM=SM+X(I,K)*ST(I,K)*4.184E-03-R*1E-06*X(I,K)*LOG(X(I,K)): REM
   kcal to MJ and J to MJ
12660 SS=SS-R*1E-06*X(I,K)*LOG(X(I,K) ): REM J TO MJ, structural part
12670 NEXT K: NEXT I
12680 SM=SM-SS: REM Instead adding the structural part to the chemical
   exergy
12690 I=0:K=0
12700 IF T=0 THEN GOTO 12710
12710 HM=HM*X
12720 SM=SM*X
12730 CF=CF+1E-10
12740 SS=(SS-R*1E-06*CF*LOG(CF) )*X: REM Correction due to the unknown
   part
12750 IF T=T0 THEN GOTO 12780
12760 HM=HM/(1-CF)
12770 SM=SM/(1-CF)
12780 EM=HM-T0*SM
12790 ES=T0*SS: REM Only the structural exergy
12800 RETURN
12810 REM
12820 REM Calculation of chemical enthalpy and exergy
12830 REM TO=298.15 K and p0=1 atm
12840 REM Ref. calculation 821209-17
12850 EC=0:HC=0
12860 FOR I=1 TO N: FOR K=0 TO 3
12870 IF X(I,K)=0 THEN GOTO 13290
12880 IK=I+.1*K
12890 H=0
12900 IF IK=1! THEN E=235.34:H=285.83:REM MJ/kmol
12910 IF IK=1.1 THEN E=0
12920 IF IK=2! THEN E=30.14166267#
12930 IF IK=6! THEN E=410.35:H=393.51
12940 IF IK=6.1 THEN E=275.14:H=282.98:REM
12950 IF IK=6.2 THEN E=19.87206245#
12960 IF IK=6.3THEN E=830.28:H=890.36
12970 IF IK=7! THEN E=.61322689#
12980 IF IK=7.1THEN E=106.73:H=82.05
12990 IF IK=8! THEN E=3.875104228#
13000 IF IK=10! THEN E=27.05788414#
13010 IF IK=11! THEN E=367.29:H=447.48
13020 IF IK=11.1 THEN E=94.87:H=85.81
13030 IF IK=11.2 THEN E=226.98:H=307.7
13040 IF IK=11.3 THEN E=1383.8:H=1656.91
13050 IF IK=13! THEN E=791.2:H=837.85
13060 IF IK=13.1 THEN E=5.83
13070 IF IK=14! THEN E=853.965:H=910.94
13080 IF IK=14.1THEN E=729.546:H=811.36
13090 IF IK=14.2 THEN E=1.167
13100 IF IK=15.1 THEN E=674.211:H=760.44
13110 IF IK=16! THEN E=1087.28:H=1209.22
```

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13120 IF IK=16.1 THEN E=790.97:H=912.39
13130 IF IK=18! THEN E=11.58510846#
13140 IF IK=20! THEN E=719.27:H=813.41
13150 IF IK=20.1 THEN E=117.17:H=178.32
13160 IF IK=20.2 THEN E=7.09
13170 IF IK=23! THEN E=716.47:H=775.3
13180 IF IK=24! THEN E=740.725:H=881.15
13190 IF IK=25! THEN E=478.079:H=520.03
13200 IF IK=25.1THEN E=117.097:H=134.81
13210 IF IK=26! THEN E=372.632:H=412.12
13220 IF IK=26.1 THEN E=128.174:H=140.16
13230 IF IK=26.2 THEN E=8.834
13240 IF IK=26.3 THEN E=110.189:H=117.98
13250 EC(I,K)=E*C(I,K)/M(I,K): REM Chemical exergy of substance I,K
13260 HC(I,K)=H*C(I,K)/M(I,K): REM Chemical enthalpyy of substance I,K
13270 EC=EC+EC(I,K)
13280 HC=HC+HC(I,K)
13290 NEXT K: NEXT I
13300 I=0: K=0: IK=0: E=0: H=0
13310 EC=EC-ES: REM Subtracting the structural exergy for ideal mixtures
13320 RETURN
13330 REM
13340 REM Printing
13350 PRINT
13360 PRINT
13370 REM Printing result with actual mass flow
13380 INPUT "Mass in kg 0 ",M
13390 PRINT "Chemical enthalpy: ",M*INT(HC*100000!+.5) 7100000!," MJ"
13400 PRINT "Thermal enthalpy: ",M*INT(HM*100000!+.5) 7100000!," MJ"
13410 PRINT "Total enthalpy: ",M*INT((HC+HM)*100000!+.5)/100000!," MJ"
13420 PRINT "Entropy: ",M*INT(SM*100000000!+.5) /100000000#," MJ/K"
13430 PRINT "Chemical exergy: ",M*INT(EC*100000!+.5) 100000!," MJ"
13440 PRINT "Structural exergy: ",M*INT(ES*100000!+.5)/100000!," MJ"
13450 PRINT "Thermal exergy: ",M*INT(EM*100000!+.5) /100000," MJ/K"
13460 PRINT "Total exergy: ",M*INT((EC+ES+EM)*100000!+.5)/100000!," MJ"
13470 RETURN
13480 REM
```