34 The Fuel Shortage and Thermodynamics— The Entropy Crisis*

JOSEPH H. KEENAN,† ELIAS P. GYFTOPOULOS,†
AND GEORGE N. HATSOPOULOS‡

34.1. Introduction

The purpose of this paper is to bring to the attention of the broad spectrum of specialists currently concerned with the energy question in the United States the necessity for using a yardstick other than energy for assessing the effectiveness of fuel usage.

In establishing present patterns of energy consumption, the standard procedure is to find the total amount of energy used in each sector of the economy and, thus, to determine the needs of each sector for different fuels. The term energy in this connection is ambiguous. For example, the heat required in an industrial process may be added to the electrical work required or to the "heating value" of the fuel consumed in producing the electrical work required. None of these quantities represents energy consumed in the process, because it is known from the first law of thermodynamics that energy, rather than being consumed in any process, is always conserved. When opportunities for fuel conservation are to be assessed, it becomes necessary to use a measure other than energy.

For example, every engineer knows that a Btu (British thermal unit) of enthalpy in the circulating water of a power plant is less marketable and less valuable than a Btu of enthalpy in a steam main. He realizes also that a cold battery that is charged is more valuable and useful than a discharged battery having the same energy by virtue of being hot.

Typical conditions of process steam used in industry are 270°F and 30 psig. The heat required to change water from ambient conditions (55°F) into typical process steam conditions is 1150 Btu per lb of steam. Accordingly, since the typical heating value of hydrocarbon fuels is about 20,000 Btu per lb of fuel, it is often concluded that 0.057 lb of fuel per lb of process steam is needed. If this amount of fuel were used then, according to the customary definition, the effectiveness of fuel utilization would be 100%. By virtue of the first and second laws of thermodynamics, on the other

---

* Invited paper presented by the last author. The text is a revised version of the lecture.

† Massachusetts Institute of Technology, Cambridge, Mass.

‡ Thermo Electron Corporation, Waltham, Mass.

hand, it can be shown that the minimum amount of fuel required to accomplish the task just cited is only 0.015 lb of fuel per lb of steam and, therefore, only when this minimum amount is consumed is the process 100% effective. Conversely, if 0.057 lb of fuel per lb of steam is consumed, the effectiveness of fuel utilization is only $0.015/0.057 = 26\%$.

The preceding simple examples illustrate the necessity for using a yardstick other than energy for assessments of fuel needs and of effectiveness of fuel utilization. The laws of thermodynamics indicate that neither energy, nor heat, nor enthalpy, nor Gibbs free energy are in general satisfactory yardsticks. The relevant quantity is a property called available useful work that is in turn uniquely related to another important property called entropy. Hence, the subtitle is chosen to be "The Entropy Crisis" in suggestive distinction to the fashionable characterization of the problem as "The Energy Crisis."

This paper is concerned with the thermodynamic arguments that lead to available useful work or entropy as the objective measure of fuel needs and of effectiveness of fuel utilization.

34.2. Available Useful Work

It was observed by Lazar Carnot about the year 1800 that the perfect hydraulic engine would produce enough work to return all the working fluid to its elevated source if that work were used in a perfect pump. Another way of saying this is that the minimum requirement for lifting water from one level to a higher one is that an equal weight must be lowered from the higher level to the lower one. Moreover, more than this minimum is required if any part of the mechanism involved is less than perfect.

Such observations are generalized in the laws of thermodynamics from which the following theorem may be proved: for any physical task that is to be performed within an environment that is essentially in a stable equilibrium state, a certain minimum of work is required. The task to be performed may be as simple as the raising of a mass of material from one level to another in the gravity field, or as complex as the conversion of iron ore into steel. The minimum work will be required when the task is performed reversibly, that is, in such a way that all systems involved in the process can be restored to their initial states after the process has occurred, leaving no physical evidence that any process had taken place.

It will be observed from the preceding theorem that the work of the reversible process is fixed by the nature of the system and the initial and final states of that system in the process. Even though the number of such possible reversible processes between the same end states may be infinitely large, the work required is identically the same for all of them.

Associated with each system in each state will be, then, an amount of work which is the minimum required to create that system in that state out of materials from the atmosphere or in mutual stable equilibrium with the atmosphere. This minimum amount is also equal to the maximum useful work that can be done by the system starting from a given state and ending in a state in mutual stable equilibrium with the atmosphere. It is called the available useful work of the system in that state.[1]

Values of available useful work are, of course, associated with the fuels we use. If a fuel such as the molecular species CH_2 were to be formed reversibly from carbon dioxide and water in the atmosphere, the work required would be the available useful work of the fuel. This work could be recovered completely for use on other systems if the fuel were combined with oxygen from the air in a reversible process that restores the carbon dioxide and water as constituents of the gaseous mixture we call air. Clearly, each task that is to be performed on any system within the atmosphere may be carried out by means of the oxidation of fuel without consuming any resource other than the infinite atmosphere, because only work is required and the oxidation of fuel is entirely equivalent in the reversible ideal process to a supply of work.

Indeed in the great majority of all physical tasks undertaken by modern American society, whether they be the lifting of a steel beam to the top of a building or the heating of a house, the process drawn upon is the oxidation of fuel. The proliferation of these tasks in an affluent society has increased the magnitude of the basic process, namely oxidation of fuel, to the point where such questions as where is the fuel to come from? how do we get it? and how do we pay for it? have resulted in what is called the energy crisis but which would be more appropriately called the fuel crisis or fuel shortage.

It is appropriate, therefore, to give thought to the minimum magnitude of the oxidation process that will permit the desired tasks to be performed —that is, the minimum fuel requirement. This minimum would be attained if the oxidation process and all subsequent operations were to be executed reversibly within the terrestrial (air and water) environment. It can be shown that the annual minimum would consume a tiny fraction of the fuel consumed in the year 1972. That tiny fraction would provide all the lifting jobs, all the metal-forming jobs, and all the industrial and domestic heating to which society is now accustomed or is likely to become accustomed in the foreseeable future.

Why then do we consume the massive quantities of fuel that we do? The answer is in part economic; namely, that we use the amount of fuel that minimizes the sum of capital and operating costs. It is also in part technological; namely, that we have not organized our technological skills so as to reduce substantially the fuel requirement.

The economic optimization usually performed by either consumer or industry is faulty. It would be valid only if the prices of capital goods and fuel reflected their total social costs. That is, the price of coal would have to include the cost of rehabilitating the landscape after strip mining, and the price of imported oil would have to reflect in some way the effect of the import on the national balance of payments. On the other hand, the price of iron and steel for power plants and other machinery would have to reflect the cost of cleaning up atmospheric and water pollution caused by production of iron and steel.

The technological argument is not, of course, entirely independent of the economic one. With proper price allocation the demand for competent engineers and engineering to reduce fuel consumption would rise considerably above present levels. As prices and social pressures for fuel conservation increase, however, engineering efforts will be more and more directed toward devising means for realizing in some degree the vast potential for reducing consumption of fuel. It is to this task that the present paper is directed.

The thermodynamic measure of the task-performing value of fuel and air or their products of oxidation is, as stated earlier, the maximum possible work, the available useful work, that could be obtained from them. The amount of this work is dependent on the temperature and other properties of the environment (ambient air and water) *to* which or *from* which the fuel-air system may *deliver* or *receive* energy in any quantity.

In a reversible process the available useful work is conserved. That is, when fuel is oxidized in order to perform a specific task on a specific material, the available useful work is merely transferred from the fuel-air system to the material if the process is executed reversibly. It is informative, therefore, to examine the performance of any particular task so as to trace the losses in available useful work that occur in each step of that task.

The available useful work Φ of a system and atmosphere can be shown to be given by the equation

$$\Phi = E + p_0V - T_0S - \sum_{i}^{n} \mu_{i0}N_i, \tag{34.1}$$

where E denotes energy, V volume, and S entropy of the system, N_i for $i = 1, 2, \ldots n$ the number of moles of molecular component i in the system, p_0 the pressure of the atmosphere, T_0 the temperature of the atmosphere, and μ_{i0} the total potential of component i in the atmosphere or in mutual stable equilibrium with it.

The quantity Φ may be evaluated for any system in any state whether stable equilibrium, nonstable equilibrium, or nonequilibrium. In particular its value is zero when system and atmosphere are in mutual stable equilibrium. That is, Φ is zero when the system is in a stable equilibrium state such that its temperature is T_0, its pressure p_0 and its total potentials are μ_{i0} for $i = 1, 2, \ldots n$.

The close relationship between the quantity Φ and the entropy is evident from Equation 34.1. For given energy, volume, and composition of the system, Φ decreases with increase in entropy of the system. For states of small entropy the available useful work is large, and vice versa. A deficiency in available useful work corresponds to a surplus of entropy. The value of Φ may exceed that of the energy of the system. It cannot, of course, exceed the energy of the system and atmosphere taken togther.

In general, the available useful work Φ is different from the Gibbs free energy Z and enthalpy H. Unlike Φ, which has a value for any state of the system, equilibrium or nonequilibrium, Z and H are defined ($\equiv$) for stable equilibrium states only, as follows:

$$Z \equiv E + pV - TS \quad \text{and} \quad H \equiv E + pV, \tag{34.2}$$

where p and T denote, respectively, pressure and temperature which are not in general identifiable for states that are not stable equilibrium states.

The available useful work Φ was devised by Gibbs (1948, p. 77, Equation 54) in 1875. In an earlier paper Gibbs (1948, p. 58) had introduced the function

$$E + p_0V - T_0S \tag{34.3}$$

for application to a system the constituent substance of which did not enter into or mix with the atmosphere. The maximum possible decrease in the value of this function as the system (body) proceeded toward pressure and temperature equilibrium with the atmosphere (medium) he called the "available energy of the body and medium." Gouy (1889) introduced the abbreviated form of Gibbs function

$$E - T_0S, \tag{34.4}$$

the change in which for any change of state is the available work Ω used to introduce the property entropy.

A closely related property

$$H - T_0S, \tag{34.5}$$

which is particularly useful for calculating the available work in steady-flow processes, was used by Darrieus (1930) for processes in turbines and by Keenan (1932) for analysis of steam power plants and for cost accounting when both process steam and power are produced. It appeared in an engineering textbook by Bosnjakovic (1935) and more recently in European literature (Brennstoff-Warme-Kraft, 1961),[2] where it has been given the name exergy.

When applied to a hydrocarbon fuel, the quantity Φ is the minimum useful work required to form the fuel in a given state from the water and carbon dioxide in the atmosphere. Since this minimum will be the useful work of a reversible process, the quantity Φ is also the maximum useful work that could be obtained by oxidation of the fuel and return of the products to the atmosphere. Moreover, any change in state of the fuel-air-atmosphere system will produce an amount of useful work less than, or in a reversible change, equal to the corresponding decrease in Φ.

34.3. Examples

The curves of Figure 34.1 are calculated for 1 pound-mole of a liquid hydrocarbon fuel which may be described as CH_2 and which has a so-called heating value of 280,000 Btu (20,000 Btu per pound). This heating value is the decrease in enthalpy when 1 pound-mole of fuel burns in theoretical air to carbon dioxide, water, and nitrogen:

$$CH_2 + \frac{3}{2}O_2 + 5.65N_2 \rightarrow CO_2 + H_2O + 5.65N_2. \tag{34.6}$$

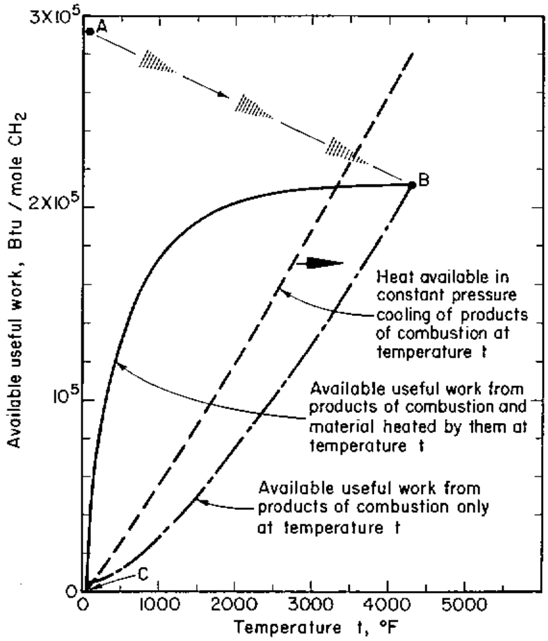

Figure 34.1. Available useful work from oxidation of CH_2 (Equation 34.1).

The available useful work for the reactants of this reaction can be shown to be about 292,000 Btu per pound-mole, namely about 4% greater than the heating value. In order to obtain this work, the following process, as one among many possible ones, could be used: (1) the oxidation is carried out in a reversible fuel cell, at some temperature T_c, which delivers electrical work to the surroundings; (2) the products of the fuel-cell process are cooled from T_c to the temperature of the environment T_0 as they provide heat to Carnot engines that produce further work; (3) each of the products CO_2, H_2O, and N_2 is separated from the mixture reversibly by means of a semipermeable membrane and expanded reversibly and isothermally at T_0 in an engine cylinder until it attains a pressure equal to the partial pressure of that constituent in the atmosphere; (4) each molecular species is introduced reversibly into the atmosphere through a semipermeable membrane. The term semipermeable membrane refers to a device that is impermeable to all molecular species except one. The final state after step (4) corresponds to zero available useful work at atmospheric temperature (55°F). It is the base state C in Figure 34.1.

Such a fuel-air process would produce the maximum possible work, the available useful work. Moreover, the work so obtained could be used in an inverse process to create the original quantity of fuel from the carbon dioxide and water vapor in the air. Any oxidation process that produced less work than the available useful work would be irreversible, and the loss in available useful work would be a measure of the irreversibility of the process.

Work is produced for use in one or more tasks. Because these tasks are almost always performed with a high degree of irreversibility, the available useful work remaining in the material operated on is usually only a small fraction, and more often a tiny fraction, of that available at the beginning of the task. When a steel beam is lifted to the top of a tall building, the available useful work remaining at the end of the task may be of the order of 10% of that in the fuel-air system that was the source of the work. In the manufacture of the steel beam, on the other hand, the available useful work remaining in the beam is a fraction several orders of magnitude less than in the lifting process. The search for potential savings of fuel, therefore, must involve, first, the oxidation process and, second, the task that uses the work produced by the process.

Because fuel cells for efficient oxidation of a hydrocarbon fuel are not presently obtainable, although they are in various stages of development, fuels are almost always burned in a combustion chamber without production of electrical current. For CH_2 and the reaction cited earlier, the temperature at the end of the combustion process is about 4300°F, the adiabatic flame temperature for the stoichiometric mixture. Being irreversible, the combustion process, which is suggested in Figure 34.1 by the broken line AB, results in an increase in entropy and a loss of available useful work. Here the loss is 80,000 Btu per pound-mole of our assumed fuel or about 27% of the original value of 292,000 Btu. The remaining available useful work is 212,000 Btu, which is the maximum amount of work that could be obtained, for example, by transferring heat to Carnot engines and by expansion of the product species to the limit imposed by the environment at C.

The combustion process A to B in Figure 34.1 is a constant-enthalpy process. That is, the capacity for solely transferring heat in steady flow to surrounding systems remains unaltered by the combustion process. By virtue of the irreversibility and the associated increase in entropy in the adiabatic combustion process available, useful work has been lost at constant enthalpy. An analogous process is the flow of a perfect gas through a throttle valve from high to low pressure. Enthalpy remains constant while entropy increases. In the throttling process available useful work is lost while temperature remains constant, whereas in the combustion process available useful work is lost while the temperature rises. Both are adiabatic processes in which entropy increases because of irreversibility.

Beginning with state B, the available useful work can be altered in a number of ways. For example, the energy of the combustion products may be transferred in the form of heat to any material at a temperature *t* less than 4300°F, and the transferred energy may be used reversibly to produce work. Because the temperature difference between the combustion products and the material is finite, the transfer process is irreversible and, therefore, the available useful work decreases. The solid curve in Figure 34.1 shows the available useful work in the products plus that in a material at temperature *t*°F which has cooled the products to *t*°F without itself changing temperature. For this purpose the material is assumed to be of infinite heat capacity because otherwise some heat would be transferred to material at temperatures less than *t*°F and the loss in Φ would be correspondingly greater. That is, the solid curve shows the maximum available work useful after cooling the products to *t*°F.

The dash curve of Figure 34.1 shows the heat available from products of combustion in simple steady-flow cooling from temperature *t* to the temperature of the atmosphere (55°F). It is indeed the variation of enthalpy with temperature. The dot-and-dash curve shows the corresponding available useful work of the products of combustion at temperature *t*. It reaches atmospheric temperature at a small positive value of the ordinate corresponding to the work obtainable upon reversibly mixing the products with the constituent gases of the atmosphere. The difference in ordinate between solid curve and dot-and-dash curve at any value of *t* is the available useful work from infinite-heat-capacity material that has cooled the products from 4300°F to *t*°F.

It is evident from the solid curve that as the temperature of the heat-receiving material is lowered below 2000°F the loss in Φ increases rapidly with decrease in temperature. At a temperature of about 600°F, the value of Φ is about 48% of that for the fuel initially or 140,000 Btu per mole of fuel.

A typical average temperature of the heat-receiving water-steam working fluid in a central steam power plant is 600°F. Accordingly about 25% of the available useful work of the fuel is lost in the irreversible process of transferring energy from the products of combustion to the working fluid across a finite temperature difference. Magnetogasdynamic and thermionic devices have been proposed to bridge these temperature differences and to salvage losses in Φ by reducing irreversibilities.

In an industrial plant, on the other hand, the products of combustion might be used to make process steam at, say, 270°F. The loss of available useful work is then 292,000 minus 90,000 or about 69% of that in the fuel. The difference between 69% and 52% (that is, 100% − 48%) represents the fraction lost because a steam power plant was not interposed between the products of combustion and the process steam. It can be shown by a simple calculation that for the same amount of process steam an interposed steam power plant may produce 60,000 Btu of electrical work for an additional 0.23 mole of fuel consumed. Thus, 60,000 Btu of electrical work would be obtained at the expense of 0.23 × 292,000 or 67,000 Btu of available useful work. A central station power plant would consume about 0.55 mole of CH_2 (as compared with 0.23) and 161,000 Btu of available useful work (as compared with 67,000) to produce the same amount of electrical work.

The preceding paragraphs discuss an example of topping a heating process with a power-producing process in order to reduce the loss of available useful work. Many industrial heating processes, on the other hand, require such high temperatures that a topping process would require either unobtainable or prohibitively expensive materials. Moreover, the saving to be realized per thousand degrees of temperature interval, as shown by the upper portion of the solid curve of Figure 34.1, is small.

In these high-temperature processes, such as the manufacture of steel or cement, emphasis should be placed on salvaging available useful work from the material in process and from the products of combustion leaving the heating process. For example, the billets leaving a heating furnace contain 15 to 50% as much potential to supply heat to other processes as the fuel originally consumed. A similar range of potential may be found in the products of combustion leaving the heating process. The opportunities for reclaiming available useful work through heat transfer to power-producing or lower-temperature heating processes are evident.

The possibilities of arranging processes in series in order to reduce consumption of fuel and available useful work in a simple industrial process may be illustrated by the distillation of seawater to make freshwater. In the best modern plants about 13 pounds of freshwater are made for the amount of fuel that would make 1 pound in a simple distillation. The effectiveness of the process in terms of available useful work produced to that consumed is still very small, but it is thirteen times as great, and the fuel consumption is one-thirteenth as great as in the simple distillation.

It has been estimated that about a quarter of the annual fuel consumption in the United States is attributable to generation of electrical work in central station power plants and another quarter to industrial process heating. In terms of loss of available useful work the central station power plant is far less wasteful than the industrial plant. The product of the power plant, which is pure available useful work, accounts for about one-third of the available useful work consumed, whereas the product of the industrial process accounts for small fractions of 1% of the available useful work consumed. The opportunities for reducing fuel consumption appear, therefore, to be far greater in industrial processing than in power production.

Engineers have been aware of these opportunities during the past century. It is a curious fact that topping of industrial heating with power production was more common 40 years ago than it is today. The reasons for this change are of such vital interest in view of present and future shortage of fuel that they should be thoroughly investigated and understood. They include, no doubt, the improved efficiency of central station power production and the relatively high cost of the licensed personnel required for the operation of a topping power plant. With more realistic pricing and controlled distribution of scarce fuel supplies, the economical practice may prove in the near future to be more nearly that of 40 years ago than that of the recent past.

34.4. Summary

A measure of fuel requirement other than the ambiguous energy or the less ambiguous enthalpy or heating value is needed. The most appropriate one is the function Φ, which was devised by Gibbs. It is the maximum useful work that can be obtained from a fuel by oxidizing it and diffusing the products of combustion into the atmosphere. This maximum will be realized in any reversible process between the initial and final conditions. Similarly, any task to be performed, such as the lifting of a steel beam or the manufacture of steel has a minimum requirement of available useful work which, when compared with the maximum obtainable from the fuel, determines the minimum amount of fuel required. Although this figure taken from current practice usually proves to be discouragingly small, it indicates the great potential in present processes for saving fuel.

Among these processes, that of the central station power plant uses fuel most effectively. Topping of process-steam units with power plants will probably return to fashion, and the corresponding bottoming of high-temperature industrial processes may come into fashion as the price of fuel comes to reflect more accurately the true economic and social cost of producing it. These are but two examples of what must become a reinvigorated engineering attack on irreversibility.

Notes

1. The adjective useful is included here because some work may be done on or by the atmosphere as the system changes volume. This part of the work is excluded from the quantity called here the available useful work. It is not excluded from another availability function which is used in the derivation of the property entropy.

2. This *Fachheft* includes, pp. 506–509, a bibliography which, although it excludes the work of Gibbs, is an excellent list for the years 1889 to 1961.

References

Bosnjakovic, Franjo (1935). *Technische Thermodynamik*, Vol. 1, p. 138, and Vol. 2, p. 2, Steinkopff, Dresden, Leipzig.

Brennstoff-Warme-Kraft (1961). *Fachheft Exergie*, Vol. 13.

Darrieus, G. (1930). *Revue Générale de l'Electricité*, Vol. 27, pp. 963–968, June 21; also *Engineering*, pp. 283–285, September 5.

Gibbs, J. W. (1948). *The Collected Works of J. Willard Gibbs*, Vol. 1, Yale University Press, New Haven, Conn., p. 77, equation (54).

Gouy, M. (1889). *Journal de Physique*, 2nd Series, Vol. VIII, pp. 501–518.

Keenan, J. H. (1932). *Mechanical Engineering*, Vol. 54, pp. 195–204, March.