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Research Article
Limits Imposed by the Second Law of Thermodynamics on Reducing Greenhouse Gas Emissions to the Atmosphere

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Abstract

Background and Objective: Society is moving toward unconventional oil and gas exploitation and greenhouse gas emissions reduction. The main objective of this research is to develop an exergy based conceptual framework that integrates all aspects of fuel production from resource extraction to environmental protection, including CO_2 abatement. **Materials and Methods:** A multistep deterministic method, from Carnot to exergy analysis, is used to develop a conceptual framework with the help of information from the literature. The approach used in this study mirrors some initial steps in the development of exergy analysis that can be found in Carnot's work, but the focus is on resource flow rather than maximum work or efficiency. The hypothesis that the flow of fossil resources to produce fuel is related to source-sink properties explored with a simple case related to heat transfer. The possible transposition of this simple case to fuel production is examined to provide insights into the possible uses of the conceptual development. **Results:** This paper proposes an exergy based conceptual source-sink approach, following Carnot's theory, to understand the complex problem of fuel production in relation to CO_2 abatement. The source is defined by natural resources and their associated quality and one sink is the atmosphere or any CO_2 confinement option. **Conclusion:** The proposed conceptual framework for source-sink exergy analysis of resource flow could improve our understanding of the thermodynamic limits and the sustainability of energy and material production.

Key words: Carnot, exergy, unconventional oil and gas, source-sink analysis, thermodynamics, fuel production, resource flow, entropy, greenhouse gas

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INTRODUCTION

A primary greenhouse gas (GHG) is CO_2 and a main source is emissions related to fossil fuel production and use. Low cost petroleum products (e.g., liquid fuel) have led over the years to the development of corresponding technologies and infrastructure. As a consequence, as conventional fossil fuels become more difficult to obtain, society seeks fuel from new sources and processes[1-4] (e.g., tar sands, unconventional oil and shale gas) compatible with new technologies. This quest might be counterproductive in terms of depletion of non-renewable resources especially when an additional objective such as reducing GHG emissions are considered.

Technology is used to extract resources and to transform them into useful products. Technology is also used or considered for pollution abatement and CO_2 confinement or treatment. Science and engineering allow the study of technology in regards to specific aspects, e.g., improvement of machines and efficiency. Exergy, which is defined as the maximum work that can be obtained from a substance or a system when it is brought into equilibrium with a reference environment, can assist such efforts. Even if one chooses a lesser environmental impact technology, high quality natural resources are becoming less available and transformation of these resources still generate environmental impacts that need to be addressed.

Second law analysis, particularly exergy analysis, can provide an integrative methodology to define the physical limits related to quality of natural resources, modern technology and pollution abatement strategies for the production of a desirable output such as fuel. This paper utilizes this characteristic of exergy and is part of ongoing research investigating the possibility to use exergy in an attempt to develop a simple method that would tie complex issues such as greenhouse gas (GHG) reduction, modern technologies, quality of natural resources and output delivered to society in relation with the flow of natural resources. The principal hypothesis/idea underlying this research is: A context of lesser quality natural resources and more stringent environmental regulation (e.g., CO_2 emission reduction) should lead to an increase natural flow of natural resources needed to deliver a desirable output to society in comparison to a context of high quality resources and no environmental constraints. If true, this hypothesis would be significant, as it would reveal a higher level of complexity related to sustainability issues and to CO_2 reduction schemes. The first step toward reaching this general objective, developing concepts and theory, is the main focus of this study.

An approach is proposed here that considers elements of theory from past to present and that is expected to help reach the initial goal of this research under a source-sink theoretical framework. This study builds on earlier study[5] in which authors investigated renewable energy under a source-sink approach where the sun was the source and the space was the sink. This approach enabled thermal and chemical cycles used to produce work to form the basis of a renewability indicator. The source-sink approach can also be considered for non-renewable energy[6] but the context is different since the source-sink system must be studied thoroughly in relation to the properties of the source and the sink. This article extends study presented earlier by the authors on the limitations imposed by the second law on reducing atmospheric GHG emissions[7].

LIMITS IMPOSED BY THE FIRST AND SECOND LAWS OF THERMODYNAMICS

Conservation of matter and conservation of energy are well known thermodynamic laws that restrict the possibilities not only to produce fuel from any energy source but also to tackle the CO_2 problem. By considering only the first law of thermodynamics and matter conservation one could be led to the conclusion that the GHG problem and the resource problem could both be solved with proper technology and financing. Matter and energy would only need to be transformed in the desired form and placed in the proper location. The first law implies that for a system defined such that only work and heat can pass through its boundaries and the only change that can occur within the system is the energy content, if no change in energy content occurs, the relationship described in Eq. 1 holds:

$$dQ = dW \tag{1}$$

where, dQ represents the incremental heat input to the system and dW the incremental work done by the system. If the heat input to this system is reduced, work output is reduced accordingly and if work is done on the system, the heat output from the system increases accordingly. The "equivalence" between work and heat is defined via Eq. 1. This relation establishes a limit to the amount of work that can be produced from heat, no more work can be done than the heat input to the system.

This limit defined by first law of thermodynamics is not the most restrictive. Equation 1 describes a relationship between work and heat when the actual transformation occurs (work to heat and heat to work) but it does not relate to the physical possibility of this transformation. Very specific conditions are required for all heat flow into the system to be transformed into work. Equation 1 does not describe this reality. Misunderstanding of this definition can lead to erroneous conclusions such as all heat content of a low temperature energy source can be converted to work. With an improper interpretation of the first law, one can conclude that it would be easy to produce energy carriers such as fuels from any energy sources.

Second law analysis can shed light on the possibilities of conversion of energy forms and exergy, a quantity based on the first and second laws, can serve this purpose. The second law of thermodynamics implies a much more complex reality and introduces a limit that is more restrictive and less frequently considered[8]. The second law is related to two natural phenomena[9], one being the transfer of heat (Carnot) and another the diffusion of molecules (Boltzmann). When unrestricted, heat passes from a hot to a cold reservoir and molecules pass from a concentrated to a more diluted state. This is nature's directional arrow, which aims only "one way." The opposite transfer, heat passing from a cold to a hot reservoir, or the concentration of dispersed molecules, needs external work. That is, exergy is needed to reduce entropy. For a specific matter/energy transformation, the second law imposes limits like the minimum work needed for these specific transformations. For instance, work is needed to extract a contaminant from a contaminated resource or CO_2 from flue gas.

CARBON DIOXIDE AND EXERGY

A few decades ago, discharging wastes in a form that is least reactive was a goal and the discharge of carbon as CO_2 was a way to achieve this objective[10]. For fossils fuels, this objective brought limited constraints to engineers since, at least in theory, complete combustion of hydrocarbons is coherent with the objective of maximizing output when for example work or electricity is produced. Efficiency improvement and CO_2 production were coherent objectives. CO_2 production is so relevant when work is desired from hydrocarbons that it serves as a reference-environment component (in the atmosphere) in the determination of chemical exergy[11]. This implies, for hydrocarbons, that CO_2 has to be produced and rejected to the atmosphere for the reactivity part of chemical exergy to be completely converted to work. Also, exergy is needed to extract from the environment and confine CO_2. But, explained below, CO_2 abatement can be counter productive with the goal of maximizing desirable output.

SOURCE-SINK APPROACH

In this paper, parts of several methods and theoretical developments are chosen to facilitate the achievement of the desired objective: Develop a new approach to address a complex problem. This research follows directly Carnot's[12] work with a focus on resource flow (e.g., carbon-based fuels) and the use of contemporary concepts such as exergy. The focus here is mainly on integrating the scientific components under a source-sink approach. The provision of energy resources to meet needs is a global problem with many facets (political, economic, technological, etc.). In a meeting in Davos[13], participants reached the following conclusion:

- "The objective of secure, reasonably priced energy and reductions in emissions of greenhouse gases (GHG) seem both out of reach and in conflict. Globally energy supplies are less secure even as emissions of greenhouse gases continue to rise. And the global risks continue to be strongly on the downside"

Research done for the US Army Corps of Engineers reached a similar conclusion regarding petroleum products[14].

- "Petroleum will remain the most strategic and political energy commodity with natural gas running a close second. There will be increasing focus on sustainability and political constraint of our current energy path-especially in the light of climate change, investment requirement and resource depletion. The situation is particularly acute in the case of petroleum"

More recently this context was introduced as follows[15].

- "Declining production from conventional oil resources has initiated a global transition to unconventional oil such as tar sands"

A source-sink approach, based on thermodynamics is proposed to tackle a very specific (but essential) aspect of this global and complex problem. Surprisingly, the situation mentioned at Davos and in the report for the US Army Corps of Engineers is founded on the science of thermodynamics and can be traced to a book by Carnot originally published in 1824[12].

Exergy is based on the pressure P, temperature T and chemical composition (represented by the mass fraction "X_i" of each constituent i) of a system and of its environment. Thus, exergy relies on a source-sink system where a flow of matter

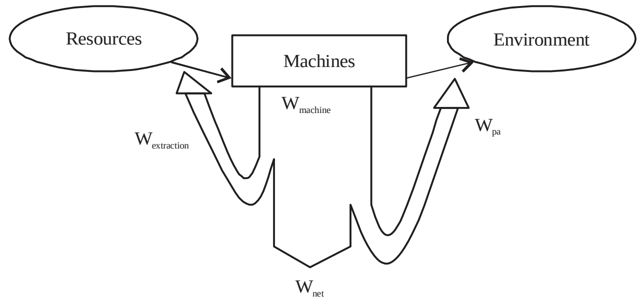

Fig. 1: Work production under a source-sink approach

and/or energy transfers between the source and the sink. In a source-sink system, aside from the desired output, matter and/or energy are generally rejected to the sink. For a thermal energy input, Carnot[12] demonstrated that heat must be rejected to a sink when work is produced. For thermal engines, when source-sink characteristics change, the theoretical maximum work that can be obtained from the system also changes[16,17]. If the atmosphere can no longer be used as a CO_2 sink, we are in effect changing the reference environment in the exergy analysis. This change affects the maximum product output (work, electricity, liquid fuels, etc.) theoretically available from the source. Consequently, in the actual quest for new energy carriers and sources, the sink is as important as the source.

Figure 1 describes a general relationship between source and sink when the source is of lesser quality and emissions to the environment must be abated. To evaluate net work output in this source-sink system, the work needed to extract the resource and for pollution abatement is deducted from the work otherwise available after a resource passes through an energy conversion device. This work (extraction and pollution abatement) could be evaluated as the minimal theoretical work (or real work) using exergy analysis. The exergy required for pollution abatement has been explored by many researchers[5,18,19]. The concept of reduction of the net output by the allocation of resources for pollution abatement is described in another study as the shrinking of the "conventional" output[20]. On the resources side presented in Fig. 1, the declining Energy Return On Investment (EROI) of fuels is a relevant example of the negative impact on the net output to society of diverting an increasing amount of resources to produce fuel[21]. The concept of work of extraction proposed here is broader than the concept of EROI that only consider energy flows. All elements, either on the resource side or the environment side, can be integrated in the proposed global approach.

A balance of the work terms in Fig. 1 yields:

$$W_{net} = W_{machine} - W_{extraction} - W_{pa} \quad (2)$$

where, W_{net} is the network available under source-sink conditions considered in Fig. 1, which differs from the conventional approach; $W_{machine}$ is the work available after a resource passes through an energy conversion device; $W_{extraction}$ is the work needed to extract the resource and process and purify it and W_{pa} is the work needed for pollution abatement. The terms $W_{extraction}$ and W_{pa} can be considered to represent a consequence of loops of internal exergy consumption in real processes. Accounting for such loops allows use of less external exergy resources when a plausible path can be considered, but the loops must be defined and used. For example, if a device produces electricity but some electricity is needed (e.g., for pollution abatement), the net electricity output is reduced. This type of approach has been used for CO_2 abatement from a thermal plant[22] using increased fuel consumption as an indicator. This approach helps to put the focus on the process considered and reduces the advantageousness of considering a process that is supported by external exergy resources.

A simple reference case can be defined where, $W_{net} = W_{machine}$ when $W_{extraction}$ and W_{pa} are negligible. Comparisons to the reference case permit the effect a modified source-sink system has on resource flow to be highlighted.

FOCUSSING ON FLOW ANALYSIS WITH CARNOT'S THEORY

Carnot[12] established the basis of the second law of thermodynamics and influenced greatly modern understanding of energy and thermodynamics, which have led to the development of exergy analysis. Carnot stated that only a fraction of a heat flow can be converted to work and that this fraction is related to the characteristics of the hot source and cold sink. This principle can be stated in a different way: When the temperatures of a source and sink are closer, a greater heat flow is needed to produce a fixed amount of work. This simple principle has broad implications.

Exergy analysis is based on the same principle, with the maximum work or exergy produced during a process related to the characteristics of the source (e.g., a natural resource) and the characteristics of the sink (the reference environment). If the characteristics of a source or sink are such that they are closer to being in thermodynamic equilibrium, less theoretical work or exergy can be produced or a greater input of exergy with matter and/or energy is required for the same product output. For two bodies at different temperatures, the closeness to equilibrium is described by their temperature difference. In exergy analysis, when chemical exergy is involved, the relationship is more complex. Exergy theory has been developed normally considering a fixed reference-environment that can be associated with a sink. This consideration simplifies the study of engineering processes[11] but it is more difficult to apply this theory when source-sink conditions changes[16]. A simplified approach is considered here to evaluate the impact of changing source-sink thermodynamic conditions.

A focus of thermodynamics in Carnot's work has been "work." This focus continues with exergy, which is defined as the maximum work available under specific source-sink conditions. Numerous efficiency definitions have developed using exergy[19,23,24]. Efficiencies generally focus on a desired output in relation to the input to a process. Thus, increasing efficiency is generally achieved by increasing the desired output and/or reducing the input. Nonetheless, undesirable outputs are produced in practice. These methods have also been used to evaluate the use of exergy by regions like countries[25,26]. Analysis of the exergy flow in countries enables to identify inefficiency in resource used by society.

Carnot's ideas permit the evaluation of the exergy of heat. By considering the work extractable reversibly from heat flowing from a hot source reservoir to a cold heat sink, the work extractable from the heat flow, which defines the exergy, can be determined as follows:

$$W = Q\frac{T_h - T_c}{T_h} \tag{3}$$

or, in terms of rates, as follows:

$$\dot{W} = \dot{Q}\frac{T_h - T_c}{T_h} \tag{4}$$

where, Q denotes the quantity of heat that passes from a hot source at temperature T_h to a cold sink at T_c and W the maximum work that can be produced from the heat flow. Also, $\dot{Q}$ denotes heat flow rate and $\dot{W}$ work production rate. These expressions show that W/Q is between 0 and 1.

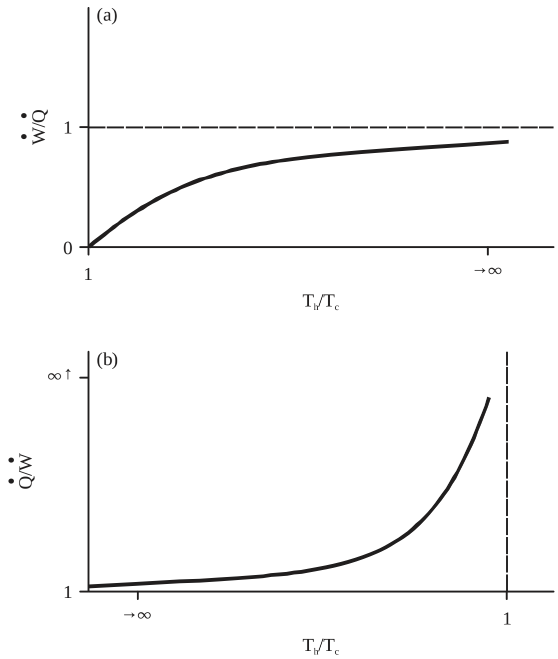

Fig. 2(a-b): Variation with temperature ratio T_h/T_c of the ratio of rates of (a) work W to heat Q and (b) heat Q to work W

By changing the focus of these equations to the flow of heat, we can write the heat flow as a function of work output and temperatures as follows:

$$Q = W\frac{T_h}{T_h - T_c} \tag{5}$$

or in terms of rates as:

$$\dot{Q} = \dot{W}\frac{T_h}{T_h - T_c} \tag{6}$$

With Eq. 5 and 6, it can be observed that Q/W or $\dot{Q}/\dot{W}$ ranges from 1 to infinity.

The ratio W/Q is often referred to as the Carnot factor and expresses the maximum work obtainable from a flow of heat from a heat source to a cold sink. Figure 2a modified from Dincer and Rosen[24] and Wall and Gong[27], illustrate this concept. Alternatively, this factor determines the minimum flow of heat needed to produce a certain amount of work for a specified source-sink system. Figure 2b, that somewhat relates to figures in Dincer and Rosen[24] and Wall and Gong[27], illustrate this different perspective. Figure 2b focuses on the heat flow needed to produce a fixed amount of work, while Fig. 2a focuses on work producible from a fixed heat flow.

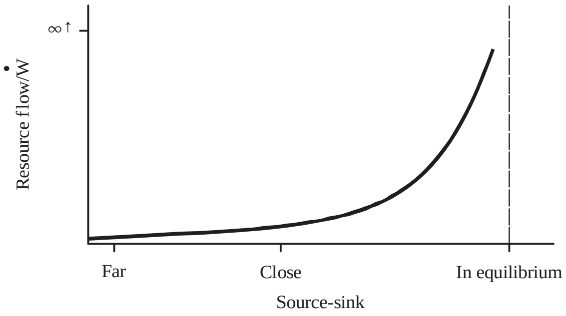

Fig. 3: Qualitative illustration of the flow of resources for a defined work output as a function of general source-sink properties

The ability to evaluate exergy efficiency with a ratio that varies between 0 and 100% (e.g., W/Q in Fig. 2a) is central in exergy analysis and leads to better understanding and quantitative information on the performance of engineering systems (e.g., heat pumps). Focussing on the inverse ratio (e.g., Q/W) could provide new scientific insights into understanding the relation between resource flow and useful output to society. Such insights could be especially useful in a context where resource flow is considered important for sustainability and environmental issues (e.g., fossil resource depletion and CO_2 emissions).

This idea could be extended with exergy to the flow of resources when a source-sink system is considered, as illustrated in Fig. 3. Shown there is a qualitative depiction of a possible variation in the flow of resources for a defined work output with source-sink properties (which need to be specified for a given factor). Under this hypothesis, when the source and the sink are considered "far" apart, a small change in the "closeness" does not have much effect on the resource flow needed to produce work. But at some point, when the source and the sink become "too close" a small change can induce a significant increase of the resource flow needed to produce work. When the source-sink are "far" apart, efficiency improvement is often the main issue to improve sustainability, but when the source and the sink are "too close", resource flow analysis could become the main issue. More research is needed to further develop the concepts represented in Fig. 3.

FLOW ANALYSIS FROM CARNOT TO MODERN EXERGY

Exergy analysis in many ways uses the same approach as Carnot's theory, but it is more general and applies to the work potential for source-sink systems due to various factors. By convention, a reference environment defines the sink. The sources are defined by thermodynamics properties (e.g., P, T, X_i). The relations among parameters and quantities for these source-sink systems involve complex definitions and mathematical relationships. As shown in the previous section, Carnot's theory can be straightforwardly rearranged to focus on heat flow required rather than work (Eq. 5 and 6). For chemical exergy such an approach would be complex and is the subject of ongoing research. In that work, at least two main difficulties need to be overcome. First, while heat is the only input flow considered by Carnot, for chemical exergy the flow of the chemical component and its reactant (e.g., oxygen) needs to be considered. Second, the reference environment in exergy analysis is often divided into three parts: atmosphere, hydrosphere and lithosphere. Matter can pass to any of the parts the reference environment, which have different compositions even though and the pressure and temperature is usually common to these three parts.

It is possible to address the minimum matter/energy flow related to a desired output in specific source-sink system without extending the mathematical relationship from Carnot's work about the minimum flow of heat. Here we consider exergy theory, which includes a reference environment. In our approach, the work (exergy) available from a resource in a reference environment is determined and the minimum work (exergy) needed to produce this resource is evaluated along with the minimum work needed to ensure that the rejected components are at the modified sink conditions (e.g., CO_2 is compressed). The work available from a specific component in modified source-sink environment can thus be evaluated.

This approach differs from that of Hermann[28], who evaluated the diffusive exergy of the CO_2 present in natural gas. In theory, work can be obtained from the CO_2 present in natural gas when it is brought to equilibrium with the atmospheric partial pressure of CO_2. In real processes, work is needed to extract CO_2 from natural gas. In this paper, the diffusive exergy of CO_2 is neglected while the work needed to extract CO_2 is considered.

FUEL

Fuels (e.g., hydrocarbons) are low-entropy energy carriers and their exergy content is close to the energy content[11]. Thus almost all of their energy content can be in theory transformed into work. Conversion of H_2 in a fuel cell is very efficient[29] and provides an example of the direct conversion of chemical exergy to work. For high-entropy energy carriers (e.g., heat at near-environment temperature), only a small fraction of the energy can be converted to work or fuels.

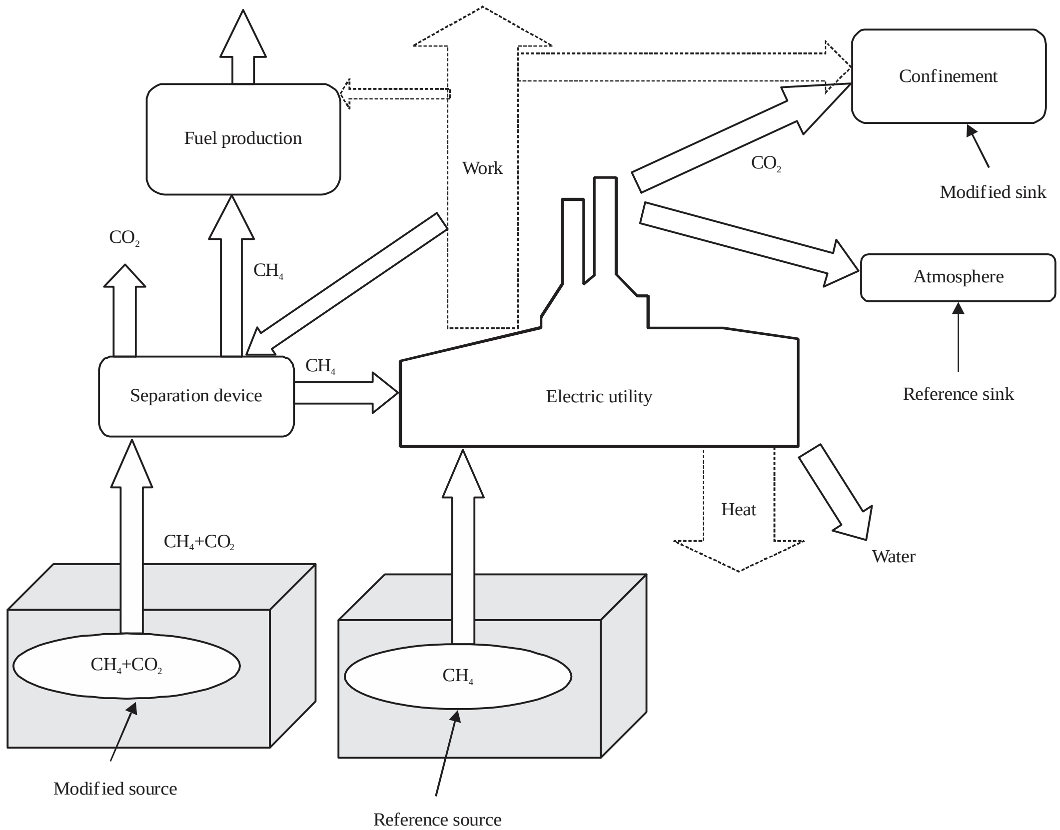

Fig. 4: Production of fuel in a modified source-sink system

Fuels are produced in a context that is changing and this context can be defined as a source-sink system. The source today is mainly non-renewable resources and one sink is the atmosphere or locations where CO_2 is stored. The minimum theoretical flow of resources needed to produce a fixed amount of fuel could dramatically increase when thermodynamics properties of the source or the sink are varied such that the effect is similar to bringing the source and the sink closer to equilibrium. A source can be considered closer to environmental conditions if it is diluted or contaminated (e.g., natural gas with CO_2 gas or other contaminants). The sink can be considered “modified” when its thermodynamic properties are different from the reference (or real) environment; this modified sink has exergy relative to the reference environment. For example, if CO_2 is compressed in order to be stored (in a modified sink), we have a situation which is equivalent to bringing the source and the sink closer to equilibrium.

An analogy can be observed by comparing with a dam. If the water level in the dam is lower, less work can be obtained from a flow of water, which is the modified source. If the level of the river below the dam is higher this also reduces the maximum work available from the flow of water, corresponding to a modified sink.

This phenomenon poses a significant challenge in reducing GHG emissions, as it leads, when the initial resource is carbon based (e.g., tar sands, unconventional petroleum), to an increase in the flow of carbon to produce the same amount of fuel. If hydrogen is produced from methane that is extracted and transformed in context of modified source-sink system (CO_2 confinement and contaminated gas at the wellhead), additional methane is needed to produce the hydrogen compared to a conventional scenario. Figure 4 illustrates the production of fuels in a modified source-sink system.

Scientific and commercial efforts to seek new energy sources should therefore be carried out simultaneously to efforts to find a cost-efficient and environmentally friendly energy sink. Separate efforts may lead to non-convergence toward the goal of reducing CO_2 in the atmosphere and may lead to increased use of natural resources.

ILLUSTRATIVE EXAMPLE: NATURAL GAS

Natural gas is available at wellhead prior to entering a pipeline with a quality that depends on the degree of contamination with a wide variety of molecules and on the source location[30,31]. The base case, which is used for comparisons with the modified source-sink conditions, is chosen to be pipeline-quality natural gas at the wellhead as the source and the atmosphere as the sink (with its chemical composition, ambient temperature and pressure). It was considered only the main constituent of natural gas, methane (CH_4), in the analysis. For the reference case, it was considered the reference environment chosen for exergy analysis. The exergy (W_0) of methane, that undergoes the following reaction, is 52.1 MJ kg^{-1} [29]:

$$CH_{4(g)}+2O_{2(g)}\rightarrow CO_{2(g)}+2H_2O_{(l)} \quad (7)$$

The thermodynamic properties of the source are described by the left side of this equation and of the sink are described by the reference environment. In this particular case the elements on the right side of the equation can be considered to be in equilibrium with the reference environment. An example of a modified source-sink system can be illustrated with a source (e.g., methane) that is mixed with another natural constituent (e.g., CO_2). The sink for one gaseous component (CO_2) is no longer the atmosphere; hence, we have a case where, $W_{extraction}$ and W_{pa} have significant values. The ideal work available in the altered source-sink condition, W_a, can be estimated as follows:

$$W_a = W_0-W_{extraction}-W_{pa} \quad (8)$$

An increased flow of resources is needed to produce a fixed amount of work in this altered source-sink system compared to the reference case. This idea allows us to write:

$$\dot{m}_a = \dot{m}_o \frac{W_0}{W_a} \quad (9)$$

where, $\dot{m}_a$ is the mass flow rate of the selected component (e.g., methane) needed in the altered condition to produce the same amount of work as the flow rate of the selected component in the pure state $\dot{m}_a$.

A brief illustration of this theory can be made with available data from the literature. Dewulf *et al.*[32] evaluated, for a specific process (on the sink side), that 5.86 MJ kg^{-1} of exergy is needed to extract CO_2 from flue gas and to compress it to 80 atm. The specific exergy of natural gas is 52.1 MJ kg^{-1}. If 1 kg of methane is combusted, the combustion reaction can be used to show that 44/16 kg of CO_2 is produced. Thus, 2.13 MJ (which represents an increase of 4.1%) of exergy is needed to abate and confine the CO_2 produced by methane combustion, leaving 49.94 MJ of exergy in the form of natural gas. If the same process could be used to extract CO_2 from natural gas at the source side, significant exergy consumption could also occur, depending on the CO_2 concentration. Moreover, if complete life cycle analysis using exergy accounting is considered, additional exergy would be consumed. For example, in the case where water pollution poses a problem[33,34], W_{pa} could be evaluated[5]. Data already available from another study[22] confirm this point. In a case where electricity is produced from natural gas, when CO_2 emissions are reduced, fuel consumption increases more than 12% to produce a fix amount of electricity compared to a thermal plant where there is no CO_2 treatment.

Data available on the sink side regarding the increased exergy consumption related to CO_2 abatement and confinement illustrate that the resource flow increase is significant only when the sink is considered. If the source side is also considered with complete exergy accounting of processes, the percentage increase in fuel use would be greater. For example, when multiple contaminants are present in natural gas, a succession of processes is needed before the natural gas becomes pipeline quality[30,35]. Each of these steps implies specific material and energy requirement in their operation. This leads to the preliminary conclusion that complete source-sink investigations are needed to address CO_2 abatement and confinement in relation to resource flow.

Figure 4 illustrates a possible source-sink condition for the production of fuel. A greater resource flow is needed to produce fuel when CO_2 is present at the source and must be confined after the resource is extracted. The minimal resource flow possible can be defined with the thermodynamic properties of the source, the sink and the fuel. Note that production of liquid fuel in altered source-sink conditions can have the same thermodynamic efficiency as the unaltered (reference) source-sink system. The increased flow of resources can remain unnoticed when focussing only on $\dot{W}$. The confined CO_2 has exergy by virtue of its purity. The confined CO_2 can be compressed although doing so increases the resource flow needed for the desired output (e.g., fuel).

IMPLICATIONS OF FLOW EVALUATION OF A SOURCE-SINK SYSTEM ON LIFE CYCLE ANALYSIS

Analyses of resource flow in variable source-sink conditions has broad implications on the results of exergetic life cycle analysis (or exergy accounting) since the size and configuration of physical devices to support that resource flow are directly related to the flow between the source and the sink. If more resources need to be transformed or processed, more pumps, larger pipes and plants and additional transportation are needed for a desired exergy output. In the extreme, the resources needed to process the flow can be more valuable (in terms of exergy and/or monetary value) than the output of the process. This lead to a fundamental question: At what point does a project become valueless to society with respect to the inputs needed to sustain it and the output it provides? Further development of the approach described in this study (an exergy-based source-sink approach) may help in resolving this uncertainty and is the subject of ongoing studies by the authors. Since exergy encompasses material and energy flows and the mineral exploitation sector is also facing lower grade deposits and increasing emissions to the environment[36], the proposed exergy based source-sink approach could be extended to the mineral sector.

In general, it is anticipated that the results will enhance understanding and the knowledge base and will also be utilizable in conjunction with related studies. Examples of related topics receiving attention in recent years include the application of thermodynamics to environmental impacts in the atmosphere[37], the utilization of exergy methods on environmental and energy problems[38], enhancing understanding of climate change[39,40] and the development of energy systems using renewable resources such as solar energy[41].

CONCLUSION

The minimum flow of resources needed to produce a desired output is a direct consequence of the limits imposed by thermodynamics. When the quality of the natural resource used characterizes a source and the different options for CO_2 emissions or confinement characterise a sink, the minimum flow of resources is linked to the thermodynamic properties of the source, the sink and the desired output(s). The fuel production process considered provides a useful example for illustrating where and how these limits should be considered. The use of carbon-based resources to produce new energy carriers (e.g., hydrogen) could be analysed with the concepts introduced in this paper to provide useful insights, prior to the implementation of an initiative.

An exergy-based method can help address the problems associated with using lesser quality resources and the consequent need for environmental protection. The method could be extended to more complex and realistic cases, e.g. the production of other fuels than natural gas, including a wide array of processes and resources (tar sands, oil shales). The source-sink approach may prove valuable in GHG reduction schemes, especially since more petroleum will be produced from unconventional sources in the future and because CO_2 capture and sequestration may be implemented. Such activities likely will lead to an increase in resources needed to produce desired outputs.

SIGNIFICANCE STATEMENTS

A thermodynamic conceptual framework is proposed to address the complexity of fuel production in the context of unconventional oil and gas exploitation and greenhouse gas reduction schemes. In comparison to conventional oil and gas exploitation, an increasing amount of material and energy must be used to produce fuel. In this context, not only could the resource flow to produce the same quantity of fuel increase significantly, but also could the material and energy needed in the process. At some point, the overall fuel production process can become useless by considering, with an exergy approach, the net output to society. The proposed conceptual framework of source-sink exergy analysis of resource flow could improve our understanding of this thermodynamic limit and the sustainability of fuel production.

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