Modeling of thermodynamic processes using the properties of matter presented in the form of spreadsheets

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Abstract. New thermodynamic cycles are developed in which the working fluid used cannot be considered as an ideal gas. This applies to oxy-fuel combustion cycles. In these cycles, oxygen is separated from the air prior to combustion. The combustion chamber is supplied with fuel and pure oxygen. The required temperature at the outlet of the combustion chamber is achieved by supplying some other substances from which it is easy to separate the CO2 formed during the combustion of the fuel. Commonly, CO\textsubscript{2}, or H\textsubscript{2}O, or their mixture is used as such substances. Thus, there are no exotic substances in the composition of the working fluid, but such a range of parameters is chosen for such cycles that the working fluid at certain points of the cycle can be both gaseous and liquid, or in a supercritical state. To model thermodynamic processes in such cycles, it is unacceptable to use the polytropic equation of ideal gases. A technique for integrating differential equations describing the state of the working fluid is proposed. This technique is based on the presentation of the thermodynamic properties of pure substances that make up the working fluid in the form of spreadsheets. The proposed technique is implemented in a software-computing module.

1. Problem Statement

Recently, a lot of work has been devoted to develop new thermodynamic cycles operating according to the oxygen-fuel technology [1–4]. The proposed cycles, along with competitive thermal efficiency, can provide practically zero emissions of harmful substances into the atmosphere, including CO\textsubscript{2}. One of the features of these cycles is that the working fluid cannot be regarded as an ideal gas. The composition of the working fluid includes CO\textsubscript{2} and H\textsubscript{2}O, and the range of operating parameters covers the regions of the gaseous phase state, supercritical, and liquid. This is specifically related the compressor-less combined cycle gas turbine CCCGT cycle [5–7]. The study of new thermodynamic cycles is associated with the modeling of elementary thermodynamic processes. The problem is that within the range under consideration, the thermodynamic parameters of the working fluid cannot be described by a simple relationship used for ideal or quasi-ideal gases (by the polytropic equation of the form $PV^n = \text{const}$, because the polytropic exponent $n$ is not constant, but strongly dependent on both pressure $P$ and on the specific volume $V$). To determine the thermodynamic properties of pure substances, a method was proposed for a quick and fairly accurate determination using spreadsheets.
[8]. This work is a continuation of a previously published work on modeling thermophysical properties of matter in the form of spreadsheets.

The aim of this work is to develop a method for describing the thermodynamic processes in a mixture of substances and a software-computing module that implements this method.

2. Method describing the thermodynamic properties of a mixture of substances, where the pure substances included in the mixture are presented in the form of spreadsheets

In the considered range of parameters, the substances included in the mixture forming the working fluid can have different phase states (gaseous, liquid, equilibrium, transition from gas to liquid and supercritical state). To model the properties of such a mixture, a number of assumptions and simplifications were made. The most significant assumptions include the following. It is assumed that the part of the working fluid in the gaseous phase is a mechanical mixture of individual gases that do not enter into any chemical reactions with each other, and obeys Dalton's law. In the presence of a part of the working fluid in the liquid phase, the solubility of substances in the gaseous phase in substances in the liquid phase is not taken into account. The part of the working fluid in the liquid phase is a mechanical mixture of individual liquids that do not enter into any chemical reactions with each other. The equilibrium phase state of each individual substance is considered as if this substance was the only one with a pressure equal to the partial pressure of this substance in the mixture. The temperature is taken to be the same for all substances included in the mixture, regardless of the phase state. Based on the tasks to be solved, the possibility of the formation of a solid phase is not considered. In those areas where the appearance of a solid phase is possible, they are calculated as if the liquid phase was supercooled without a phase transition.

Taking into account the accepted assumptions, the state of pure substances is described by the spreadsheets [8]:

$$Z_j(D_{g_j}, D_{l_j}, V_{g_j}, V_{l_j}, I_{g_j}, I_{l_j}, \ldots) = f(P_j, T_j),$$

where:
- $Z$ - vector of dynamic parameters;
- $D$ - mass fraction;
- $V$ - specific volume;
- $I$ – enthalpy, but not limited by the listed parameters;
- $P$ and $T$ - pressure and temperature, respectively (also included in the $Z$ vector);
- $g$ and $l$ - respectively indicate the gaseous or liquid phase;
- $j$ - the sequence number of the pure substance included in the mixture.

To describe the state of the mixture, based on the assumptions made, a number of other equations can be written. The enthalpy of the mixture is equal to the sum of the enthalpies of all components of the mixture, which can be expressed by equation the following equation:

$$I = \sum_{j=1}^{m} (I_{g_j} \cdot D_{g_j}) + \sum_{j=1}^{m} (I_{l_j} \cdot D_{l_j});$$

(2)

The pressure of the mixture is equal to the sum of the partial pressures of all substances included in the mixture:

$$P = \sum_{j=1}^{m} P_j;$$

(3)

The temperature of all substances included in the mixture is equal to the total temperature for the mixture:

$$T_j = T;$$

(4)
Specific volume can be represented by the following equation:

\[ V = \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right) / m + \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right), \tag{5} \]

where \( m \) - the number of pure substances in the mixture.

Combining equations (1) - (5), we obtain a system of equations describing the state of the mixture:

\[
\begin{align*}
I &= \sum_{j=1}^{m} \left( I_{ij} \cdot D_{ij} \right) + \sum_{j=1}^{m} \left( I_{ij} \cdot D_{ij} \right) \\
P &= \sum_{j=1}^{m} P_j \\
T_j &= T \\
V &= \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right) / m + \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right) \\
Z_j &= f(P_j, T_j)
\end{align*}
\tag{6}
\]

This is a complex system of nonlinear equations in an implicit form, the solution of which is complicated by the fact that not all partial derivatives are continuous functions. For example, \( \partial I / \partial T \) for pure matter at the boundary of the phase transition goes from a finite value to infinity. This system of equations is solved by a numerical method. A fast convergence process was achieved due to the fact that the first action determines in which region the roots of this equation are located. Four possible areas are considered. The first area, when all substances included in the mixture are only in the gaseous phase. The second area is when all substances included in the mixture are only in the liquid phase. The third area is when at least one of the substances included in the mixture is in equilibrium and has both liquid and gaseous phases. And the fourth area, when all substances included in the mixture are in a supercritical state. Within each of the selected areas, good convergence is ensured by Newton's method.

By a thermodynamic process we mean a transition from one state to another. The fundamental for the transient process is the equation of conservation of energy (the first law of thermodynamics), which can be written in differential form as follows:

\[ dU + P \cdot dV + dQ = 0, \tag{7} \]

where \( U \) - internal energy; \( Q \) - external heat input.

Combining the system of equations (6) with the differential equation (7), we obtain the differential-algebraic system of equations (8), which simulates the thermodynamic processes of the mixture:

\[
\begin{align*}
I &= \sum_{j=1}^{m} \left( I_{ij} \cdot D_{ij} \right) + \sum_{j=1}^{m} \left( I_{ij} \cdot D_{ij} \right) \\
P &= \sum_{j=1}^{m} P_j \\
T_j &= T \\
V &= \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right) / m + \sum_{j=1}^{m} \left( \frac{V_{ij}}{D_{ij}} \right) \\
Z_j &= f(P_j, T_j) \\
dU + P \cdot dV + dQ &= 0
\end{align*}
\tag{8}
\]
For unambiguity, an additional condition is imposed that determines the thermodynamic process. For example, for an adiabatic process \( dQ = 0 \). From a practical point of view, the most interesting is the process in which part of the work done is converted into heat. This condition can be expressed by the following equation:

\[
dQ = (1 - \eta_n) \cdot P \cdot dV,
\]

where \( \eta_n \) - process efficiency (a measure of the irreversibility of the process).

In addition to the condition that determines the thermodynamic process, to integrate the system of equations (8), it is necessary to set the initial conditions (the minimum of parameters that uniquely determine the state of the mixture of substances at the beginning of the process) and the range of integration, for example, in the case of an adiabatic increase in pressure, the degree of pressure increase. Integration of equations (8) is performed by the numerical Runge-Kutta method. The required integration accuracy is achieved due to a small integration step.

The proposed method for modeling thermodynamic processes using the properties of substances, presented in the form of spreadsheets, and a computational module were developed for use in a software and computing complex that simulates power plants made according to the CCCGT cycle. But the developed computational module can be used in any computational program that uses the thermophysical properties of various substances in its calculations. This module is especially interesting for modeling installations in which the working fluid has phase transitions. Such installations include compressors with wet compression. In such compressors, in the process of increasing the pressure, a liquid is supplied to the compressed medium, which evaporates. Due to evaporation, the temperature of the pressure increase process approaches a constant value (the pressure increase process is isothermal). In addition, a phase transition is observed in the stages of steam turbines operating in wet steam.

Conclusions
A method is proposed for determining the parameters of the state of a working fluid consisting of a mixture of substances. In this case, the description of the pure substances that make up the working fluid is made in the form of spreadsheets. A technique is proposed for modeling thermodynamic processes using the properties of substances presented in the form of spreadsheets (integrating the transition process from one thermodynamic state to another). The proposed techniques are implemented in the form of software and computational modules. The developed software and computational modules are primarily intended for operation as part of computing systems that simulate power plants based on the oxygen-fuel technology. In particular, for the study of power plants based on the CCCGT cycle. However, they can be effectively used where the working fluid cannot be described as an ideal gas. Examples of such cases include wet compression plants (where the pressurization process is insulated by liquid evaporation) or steam turbine stages operating on wet steam.

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