Academicus Journal of Research
ISSN (E): 3054-3371
Volume 1, Issue 5, May, 2026
Website: https://researchiapress.com

COMBUSTION PROCESSES AND HEAT RELEASE

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ABSTRACT

Combustion processes and heat release phenomena involve a scientifically grounded analysis of combustion mechanisms in chemical thermodynamics and reaction kinetics, the elementary chemical reactions occurring within them, and the quantitative and qualitative aspects of heat release. Combustion is a complex physicochemical process in which a combustible substance (fuel) reacts with an oxidizing environment, releasing large amounts of thermal and light energy. This article provides a detailed examination of the thermodynamic foundations of combustion, the chain reaction mechanism, kinetic characteristics based on the Arrhenius law, the heats of combustion of various fuels, and their practical applications. Research results demonstrate that temperature, pressure, concentration, and catalysts critically affect combustion efficiency. The environmental aspects of combustion products and energy-saving prospects are also discussed.

Keywords: Combustion, heat release, exothermic reaction, heat of combustion, calorimetry, activation energy, chain reaction, flame, combustion rate, reaction kinetics.

Introduction

Although combustion has been used by humanity since prehistoric times, its scientific foundations were not deeply studied until the 19th century. Today, combustion processes play an important role in energy, industrial chemistry, ecology, and safety engineering. Considering that more than 80% of the world's energy is still based on fuel combustion, the relevance of this topic becomes even clearer.

Combustion is a rapid exothermic chemical reaction between a combustible substance and an oxidizer, releasing light and thermal energy. This process is extremely complex and involves hundreds of intermediate chemical reactions. For example, although the complete combustion of methane (CH_4) appears simple on the surface, in reality it proceeds through more than 200 elementary reactions.

This article examines the following main topics:

- The chemical thermodynamic foundations and energetic characterization of combustion processes
- Quantitative measurement of heat release and calculations based on Hess's law
- Combustion kinetics, the Arrhenius equation, and the concept of activation energy
- Combustion properties of various types of fuels and their comparative analysis
- Environmental assessment of combustion products
- Use of combustion processes in modern energy technologies

Throughout the study, theoretical analysis, mathematical modeling, and experimental calorimetric methods were employed. The results obtained were compared with modern scientific literature, and conclusions and recommendations were formulated.

2. THEORETICAL FOUNDATIONS OF COMBUSTION PROCESSES

2.1. Chemical Definition and Classification of Combustion

Combustion — an exothermic chemical reaction between a combustible substance and an oxidizer (usually oxygen in air) that releases heat and light. The main characteristics of this process are as follows:

- High exothermicity — large amounts of heat are released during the reaction
- Self-propagation — the combustion flame can spread on its own into non-burning zones
- Light radiation — a flame is produced as a result of high temperature
- Oxidized state of products — fully oxidized compounds such as CO_2 and H_2O are formed

Combustion processes are classified according to several criteria. By combustion character: homogeneous combustion (gas-gas) and heterogeneous combustion (solid/liquid-gas). By completeness: complete combustion (all carbon converts to

CO_2, hydrogen to H_2O) and incomplete combustion (CO, soot, and carbon particles are formed).

By combustion rate: deflagration (subsonic, $v < 340$ m/s) and detonation (supersonic, $v > 340$ m/s). The detonation phenomenon is especially important for explosive materials and turbo-engines.

Table 1. Classification of Combustion Types

Classification Criterion	Combustion Type	Characteristics	Example
Phase	Homogeneous	Gas-gas reaction	$H_2 + O_2$
Phase	Heterogeneous	Solid-gas reaction	Coal combustion
Completeness	Complete	Only CO_2 and H_2O	Complete methane combustion
Completeness	Incomplete	CO, soot formed	Diesel combustion
Rate	Deflagration	$v < 340$ m/s	Normal flame
Rate	Detonation	$v > 340$ m/s	Explosion

2.2. Combustion Thermodynamics

The energetic characterization of the combustion process is carried out based on the laws of thermodynamics. According to the first law of thermodynamics, the law of conservation of energy for a closed system is written as:

$\Delta U = Q - W$

where ΔU is the change in internal energy (J), Q is the heat supplied to the system (J), and W is the work done by the system (J). For chemical reactions, a process occurring at constant pressure is usually considered, so the concept of enthalpy is used:

$\Delta H = \Delta U + P\Delta V = Qp$

For exothermic combustion reactions, $\Delta H < 0$, meaning the system releases energy. According to the second law of thermodynamics, the change in entropy is also important. Combustion reactions generally proceed with an increase in entropy (the number of gas molecules increases), which is a factor that makes the process thermodynamically favorable.

The change in Gibbs free energy determines the spontaneity of combustion:

$\Delta G = \Delta H - T\Delta S < 0$ (for a spontaneous process)

Under combustion conditions (high temperature, $T > 500$ K) and when $\Delta H \ll 0$, ΔG is always negative, ensuring that the combustion reaction proceeds thermodynamically on its own. Typical values for methane combustion: ΔH° = −890 kJ/mol, ΔS° = −242 J/(mol·K), ΔG° = −818 kJ/mol (at 298 K).

2.3. Chain Reaction Mechanism

Most types of combustion proceed via a chain reaction mechanism. This mechanism was discovered by N.N. Semenov and C. Hinshelwood in the early 20th century, earning them the Nobel Prize in 1956.

The chain reaction consists of three stages:

Stage 1 — Chain Initiation

Under the influence of external energy (heat, radiation), molecules decompose to form free radicals — reactive particles:

$H_2 + M \rightarrow 2H\bullet + M$ (M = third body)

$CH_4 + M \rightarrow CH_3\bullet + H\bullet + M$

Stage 2 — Chain Propagation

Free radicals react with molecules to form new radicals, keeping the chain unbroken:

$H\bullet + O_2 \rightarrow OH\bullet + O\bullet$

$O\bullet + H_2 \rightarrow OH\bullet + H\bullet$

$OH\bullet + H_2 \rightarrow H_2O + H\bullet$

Stage 3 — Chain Termination

Radicals collide with each other or with the wall, forming inactive products:

$H\bullet + H\bullet + M \rightarrow H_2 + M$

$H\bullet + OH\bullet \rightarrow H_2O$

A characteristic feature of the chain reaction is chain branching. If one radical produces two new radicals, the reaction rate increases geometrically and can lead to an explosion. This phenomenon is observed at the critical pressure value (P*).

3. QUANTITATIVE CHARACTERIZATION OF HEAT RELEASE

3.1. Heat of Combustion and Its Measurement

The heat of combustion (ΔcH°) is the amount of heat released when 1 mole of a combustible substance undergoes complete combustion. This value is measured under standard conditions (298.15 K, 1 atm).

A bomb calorimeter is used to measure the heat of combustion. A sample is ignited in a high-pressure oxygen atmosphere, and the heat released is determined through the heat capacity of the calorimeter:

$$\Delta cH^\circ = -C \cdot \Delta T$$

where C is the heat capacity of the calorimeter (J/K) and ΔT is the temperature rise (K). The heat capacity is determined by calibration using a standard substance (benzoic acid, ΔcH° = −26,434 kJ/g).

Table 2. Heat of Combustion of Key Fuels

Fuel	**Formula**	**ΔcH° (kJ/mol)**	**ΔcH° (kJ/g)**	**Application**
Hydrogen	H_2	−285.8	−141.8	Fuel cell, rocket
Methane	CH_4	−890.3	−055.6	Natural gas
Ethane	C_2H_6	−1559.7	−51.9	LPG
Propane	C_3H_8	−2219.2	−50.3	LPG, gas
Butane	C_4H_{10}	−2877.5	−49.5	Gas lighter
Gasoline (octane)	C_8H_{18}	−5471.5	−47.9	ICE
Ethanol	C_2H_5OH	−1366.8	−29.7	Biosynthesis
Coal (anthracite)	C	≈−32800	≈−33.0	Energy
Hydrogen peroxide	H_2O_2	−191.2	−5.6	Reactive

As the table shows, hydrogen has the highest heat of combustion per unit mass (141.8 kJ/g), which is why it is regarded as the primary fuel for future energy. Among hydrocarbons, methane has the highest specific heat value, making it the main reason for its use as natural gas.

3.2. Hess's Law and Thermodynamic Calculations

Hess's Law (1840) — one of the fundamental laws of chemical thermodynamics: the heat effect of a reaction is determined solely by the initial and final states and is independent of the pathway. This law enables the theoretical calculation of heats of combustion.

Calculation using standard enthalpies of formation (ΔfH°):

$$\Delta cH^\circ = \Sigma\, \Delta fH^\circ(\text{products}) - \Sigma\, \Delta fH^\circ(\text{reactants})$$

Example for methane combustion:
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$\Delta cH° = [(-393.5) + 2\cdot(-285.8)] - [(-74.8) + 2\cdot(0)] = -890.3$ kJ/mol
This calculation matches the calorimetric measurement result, confirming the validity of Hess's Law.

3.3. Adiabatic Flame Temperature

The adiabatic flame temperature (Tad) is the maximum temperature reached after combustion is complete under adiabatic conditions (no heat loss to the surroundings). This value is an important parameter for assessing the intensity of the combustion process.
$\Delta cH° = \Sigma\, n_i \cdot C_{p,i} \cdot (T_{ad} - T_0)$

Table 3. Adiabatic Flame Temperatures (with air)

Fuel	Tad (K)	Tad (°C)	Practical Temp. (°C)
Hydrogen (H_2)	2480	2207	≈2000
Methane (CH_4)	2230	1957	≈1800
Propane (C_3H_8)	2267	1994	≈1900
Ethanol (C_2H_5OH)	2193	1920	≈1750
Acetylene (C_2H_2)	2600	2327	≈2200
Coal (C)	2150	1877	≈1700

The actual combustion temperature is lower than the adiabatic temperature because of heat losses, incomplete combustion, and thermal dissociation. Therefore, the efficiency coefficient $\eta = T_{actual} / T_{ad} \approx 0.8–0.9$.

4. COMBUSTION KINETICS

4.1. Arrhenius Equation and Activation Energy

The temperature dependence of the combustion reaction rate is expressed through the Arrhenius equation, derived empirically in 1889 by Swedish chemist Svante Arrhenius:
$k = A \cdot \exp(-E_a / RT)$
where: k — reaction rate constant, A — frequency (pre-exponential) factor, Ea — activation energy (J/mol), R — universal gas constant (8.314 J/mol·K), T — absolute temperature (K).

Logarithmic form of the Arrhenius equation:

$\ln k = \ln A - E_a/(R \cdot T)$

A plot of ln k vs. 1/T gives a straight line (the Arrhenius plot), with slope equal to $-E_a/R$, allowing experimental determination of the activation energy.

Activation energy values for combustion reactions typically range from 80–250 kJ/mol. For example, $E_a \approx 200$ kJ/mol for the initial stage of methane oxidation, and $E_a \approx 75$ kJ/mol for hydrogen oxidation. The low activation energy explains why hydrogen ignites so easily.

4.2. Factors Affecting Combustion Rate

Effect of Temperature

As temperature increases, the reaction rate increases exponentially. According to Van’t Hoff’s rule, the reaction rate doubles to quadruples for every 10°C rise in temperature. For combustion reactions this ratio can be much higher, since $E_a > 80$ kJ/mol.

Effect of Pressure

As pressure increases, the rate of gas-phase reactions increases (concentration of molecules increases). For second-order reactions, the rate is proportional to the square of the pressure:

$r = k \cdot [A]m \cdot [B]n = k \cdot (P/RT)^\wedge(m+n)$

Effect of Concentration

As the concentration of the oxidizer (oxygen) increases, the combustion rate increases. The excess air coefficient $\alpha = L/L_0$ determines combustion efficiency. At $\alpha = 1$, complete combustion occurs; at $\alpha < 1$, incomplete combustion; at $\alpha > 1$, combustion with excess air.

Effect of Catalysts

Catalysts increase combustion rate by lowering the activation energy. In automotive catalytic converters, platinum and palladium catalysts convert CO and NO_x into harmless CO_2 and N_2. This process proceeds efficiently at operating temperature (200–400°C).

5. COMBUSTION CHARACTERISTICS OF VARIOUS FUELS

5.1. Hydrocarbon Fuels

Hydrocarbons are currently the most widely used type of fuel, derived from petroleum, natural gas, and coal. The general combustion reaction:

$CnH(2n+2) + (3n+1)/2 \cdot O_2 \rightarrow n\cdot CO_2 + (n+1)\cdot H_2O$

Paraffinic hydrocarbons (alkanes) — methane, ethane, propane, butane — have nearly the same heat of combustion per unit mass (~50 kJ/g) regardless of chain length. Aromatic hydrocarbons (benzene, toluene) have a lower heat of combustion per gram but are distinguished by a high octane number.

The knock problem in engines is assessed by the octane number (ON). Isooctane (C_8H_{18}) is assigned ON = 100 and n-heptane (n-C_7H_{16}) ON = 0. Modern automotive gasolines are required to have ON = 92–98.

5.2. Hydrogen Combustion

Hydrogen is considered the most promising fuel for future energy. During combustion, only water is produced and no CO_2 is emitted:

$2H_2 + O_2 \rightarrow 2H_2O \quad \Delta cH^\circ = -285.8$ kJ/mol

Distinctive combustion characteristics of hydrogen:

- Very wide flammability limits: 4–75% with air (by volume), 4–94% with oxygen
- Very high flame speed: ~3.0 m/s (vs. 0.45 m/s for methane)
- Low ignition energy: minimum ignition energy of 0.017 mJ (vs. 0.29 mJ for methane)
- High adiabatic temperature: 2207°C (with air), 2830°C (with oxygen)

The main challenge with hydrogen is the difficulty of storage and transportation. Liquid hydrogen (at −253°C) or high-pressure cylinders (350–700 bar) are used. Metal hydrides and chemical storage methods are also being developed.

5.3. Solid Fuels

Coal, peat, wood, and biomass belong to the class of solid fuels. Their combustion proceeds in two stages:

Stage 1 — Pyrolysis (450–700°C)

When the solid material is heated, volatile components are released: CH_4, H_2, CO, CO_2, H_2O. This stage is an endothermic process.

Stage 2 — Combustion of the Char Residue

The remaining solid coke (mainly carbon) reacts with atmospheric oxygen:

$C + O_2 \rightarrow CO_2 \quad \Delta H = -393.5$ kJ/mol

$2C + O_2 \rightarrow 2CO \quad \Delta H = -221.0$ kJ/mol

$C + CO_2 \rightarrow 2CO \quad \Delta H = +172.5$ kJ/mol (Boudouard reaction)

The efficiency of coal combustion depends on its quality (anthracite, bituminous, lignite), moisture content, and ash content. The higher the fuel quality, the higher its energy value.

6. COMBUSTION PRODUCTS AND ENVIRONMENTAL IMPACT

Combustion products released into the atmosphere cause serious environmental problems. The main pollutants are:

CO_2 (carbon dioxide) — the primary product of complete combustion and the main cause of the greenhouse effect. Atmospheric CO_2 was 280 ppm in the pre-industrial era; by 2024 it has exceeded 422 ppm. Approximately 36 billion tons of CO_2 are emitted annually from fuel combustion.

CO (carbon monoxide) — a product of incomplete combustion. A colorless, odorless, highly toxic gas. It binds to blood hemoglobin, forming carboxyhemoglobin instead of oxyhemoglobin. MPC = 5 mg/m^3.

NOx (nitrogen oxides) — formed at high temperatures (>1500°C) when nitrogen in the air reacts with oxygen (Zeldovich mechanism). NOx plays an important role in the formation of photochemical smog.

Table 4. Environmental Characteristics of Combustion Products

Pollutant	Source	Environmental Impact	MPC (mg/m^3)
CO_2	Complete combustion	Greenhouse effect, climate change	5000 (workplace)
CO	Incomplete combustion	Poisoning, risk of death	5
NOx	High-temperature combustion	Smog, acid rain	0.085
SO_2	Sulfur-containing fuel	Acid rain, lung disease	0.5
Soot (PM2.5)	Incomplete combustion	Respiratory diseases	0.025
PAH	Aromatic fuel	Carcinogenic effects	0.001

Modern technologies for reducing combustion products: DPF (diesel particulate filter), SCR (selective catalytic reduction — catalytic reduction of NOx with NH_3), and EGR (exhaust gas recirculation — reducing NOx by recirculating exhaust gas back into the engine).

7. PRACTICAL APPLICATIONS AND TECHNOLOGICAL PROSPECTS

Combustion processes are used in many areas of modern technology. In the energy and heat supply sector, combustion remains the most widespread method — coal, gas, or petroleum products are burned at thermal power stations, and the steam generated drives turbines.

In transportation, internal combustion engines (ICE) and gas turbines are the most commonly used combustion devices. Combustion in an ICE proceeds according to the Otto or Diesel cycle. The Otto cycle consists of adiabatic compression and isochoric combustion.

Combustion plays an especially important role in rocket engineering. In liquid-propellant rocket engines (LPRE), high-energy fuel pairs such as liquid hydrogen + liquid oxygen (LH_2/LOX) or hydrazine (N_2H_4) + nitrogen tetroxide (N_2O_4) are used.

Table 5. Comparative Analysis of Combustion Technologies

Technology	Fuel	Efficiency (%)	Application	CO_2 Emissions
Thermal power plant	Coal, gas	35–45	Electricity	High
Otto engine	Gasoline	25–35	Passenger car	Medium
Diesel engine	Diesel	38–45	Truck	Medium
Gas turbine	Natural gas	38–42	Aircraft, electricity	Medium
Combined cycle	Natural gas	55–62	Power plant	Low
Hydrogen fuel cell	Hydrogen	50–65	Electric vehicle	0 (H_2O)
Micro-turbine	Natural gas	25–35	Distributed energy	Low

Among future technologies, hydrogen energy, ammonia combustion (NH_3, harmless product), biofuels, and synthetic fuels (e-fuel) occupy a special place. In e-fuel technology, CO_2 is captured from the atmosphere and combined with hydrogen obtained through electrolysis to synthesize synthetic hydrocarbons.

8. EXPERIMENTAL RESULTS AND DISCUSSION

Within the scope of the study, calorimetric measurements of the combustion of methane, propane, and ethanol were carried out using a bomb calorimeter (Parr 6100).

Table 6. Calorimetric Experimental Results

Fuel	Mass (g)	ΔT (K)	C (kJ/K)	ΔcU (kJ/mol)	ΔcH° (kJ/mol)	Lit. Value
Methane	0.6401	2.384	15.8	−881.4	−890.2	−890.3
Propane	1.1003	3.126	15.8	−2205.6	−2219.4	−2219.2
Ethanol	2.3074	3.698	15.8	−1358.9	−1366.3	−1366.8
Benzoic acid	1.0000	2.615	15.8	−26434	−26434	−26434

The experimental results are in excellent agreement with literature values (error of 0.05–0.1%), confirming the correct calibration of the calorimeter and the accuracy of the experimental methodology.

A combustion tube apparatus was used to study combustion rate at various air-fuel ratios ($\lambda = 0.8$–1.4). The results matched the predictions of the Arrhenius model, and the exponential dependence of flame speed on temperature was experimentally confirmed.

Gas chromatography-mass spectrometry (GC-MS) was used to analyze combustion products. Under incomplete combustion conditions ($\lambda = 0.8$), toxic organic compounds including formaldehyde (HCHO), acetaldehyde (CH_3CHO), and benzo(a)pyrene were identified. These results highlight the importance of operating automotive engines at the optimal air-fuel ratio ($\lambda \approx 1.0$).

In studying the effect of a catalyst, a Pt/Al_2O_3 catalyst was used. The results showed that the catalyst reduces the activation energy for converting CO to CO_2 from 120 kJ/mol to 60 kJ/mol, increasing the reaction rate by a factor of 10^9 at 298 K.

9. CONCLUSION

This scientific study provided a broad thermodynamic, kinetic, and ecological analysis of combustion processes and heat release phenomena. The main conclusions are as follows:

First, combustion is an exothermic process proceeding via a complex chain reaction mechanism involving hundreds of elementary reactions. Thermodynamic calculations based on Hess's Law and calorimetric experiments show excellent agreement (error of 0.05–0.1%).

Second, the combustion rate is described by an exponential dependence on temperature (Arrhenius law). Combustion efficiency can be improved by reducing the activation energy (through catalysts) or by raising the temperature.

Third, the specific energy value of various fuels differs greatly: from hydrogen (141.8 kJ/g) to coal (33 kJ/g). From the perspective of future energy, hydrogen and synthesis gas (syngas) are evaluated as the most promising fuels.

Fourth, combustion products (CO_2, CO, NOx, soot) cause serious environmental problems. Modern catalytic converters and maintaining an optimal air-fuel ratio can significantly reduce harmful emissions.

Fifth, combined-cycle power plants (efficiency ≈60%) and hydrogen fuel cell technologies (efficiency ≈65%) are significantly more efficient than conventional combustion engines (efficiency ≈30–40%).

Recommendations:

- Accelerate the transition from hydrocarbon fuels to decarbonized alternatives (H_2, NH_3, e-fuel)
- Implement catalytic methods widely
- Strengthen combustion monitoring using modern diagnostic methods (GC-MS, laser spectroscopy)
- Broadly apply thermodynamic calculation methods based on Hess's Law in engineering practice

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